Supporting Information

Heterolytic CH Activation with a Cyclometalated Platinum (II) 6-Phenyl-4,4'-di-tert-butyl,-2,2-Bipyridine Complex.

Kenneth J. H. Young[†], Steven K. Meier[†], Jason M. Gonzales[‡], Jonas Oxgaard[‡], William A. Goddard III[‡], Roy A. Periana[†] *

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Experimental:

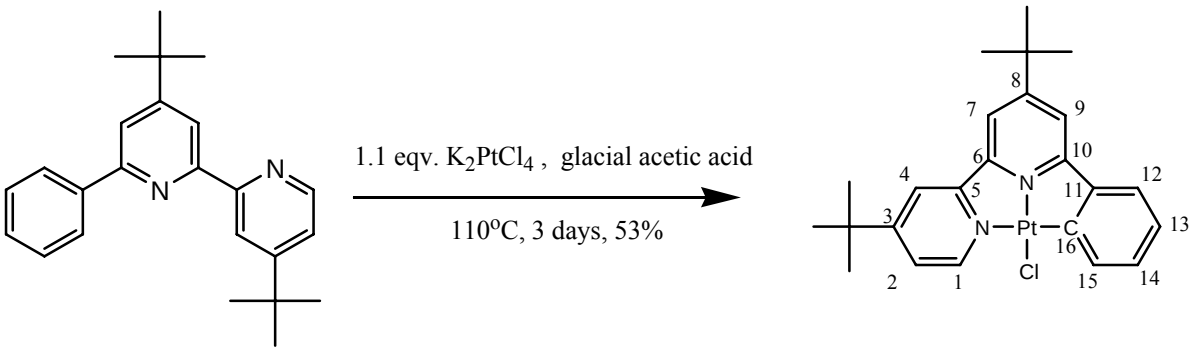
General Considerations: Unless otherwise noted all reactions were performed using standard Schlenk techniques (argon) or in a MBraun glove box (nitrogen). GC/MS analyses were performed on a Shimadzu GC-MS QP5000 (ver. 2) equipped with a cross-linked methyl silicone gum capillary column (DB5) and GS-gaspro column. ^{1}H and ^{13}C NMR spectra were collected on a Varian 400 Mercury plus Spectrometers. Chemical shifts were referenced to TMS using residual protiated solvent. ^{19}F Chemical shifts were referenced to $CFCl_3$. All coupling constants are reported in Hz. Mass spectroscopic analyses were performed at UCLA mass spec lab. Elemental analyses were performed by Desert Analytical Laboratory, Inc.; Arizona. X-ray data was collected on a Bruker SMART APEX CCD diffractometer.

Materials: K_2PtCl_4 (Strem), 4,4'-di-tert-butyl-2,2'-dipyridyl(Aldrich), Phenyllithium (1.8M in di-n-butylether, Aldrich) were used as received. All solvents were reagent grade or better. Trifluoroacetic acid-D1 (CIL) was used as received and was degassed by freeze-pump-thaw cycles prior to use. Diethyl ether was dried over sodium/benzophenone ketyl and distilled under argon. Dichloromethane (stabilizer removed with sulfuric acid) was dried over P_2O_5 and distilled under argon. 6-Phenyl-4,4'-di-

tert-butyl-2,2'-bipyridine was prepared following literature procedures.[1] Hunig's base (diisopropylethyl amine) was distilled and degassed by several freeze-pump-thaw cycles prior to use.

DFT Calculations: All theoretical calculations were performed with the B3LYP[2,3] density functional, in combination with the Jaguar 6.0[4,5] computational package. Platinum was described with the effective core potential of Hay and Wadt[6] while all other atoms used the 6-31G**[2] all electron basis set. The effects of diffuse functions were included with single point calculations. Solvation effects, in trifluoroacetic acid, (computed via single point corrections) were modeled implicitly with the PCM[7,8] model ($\varepsilon = 8.55$, solvent radius = 2.451).

Synthesis of Pt(4,4'-tBu_2(NNC))Cl (1):



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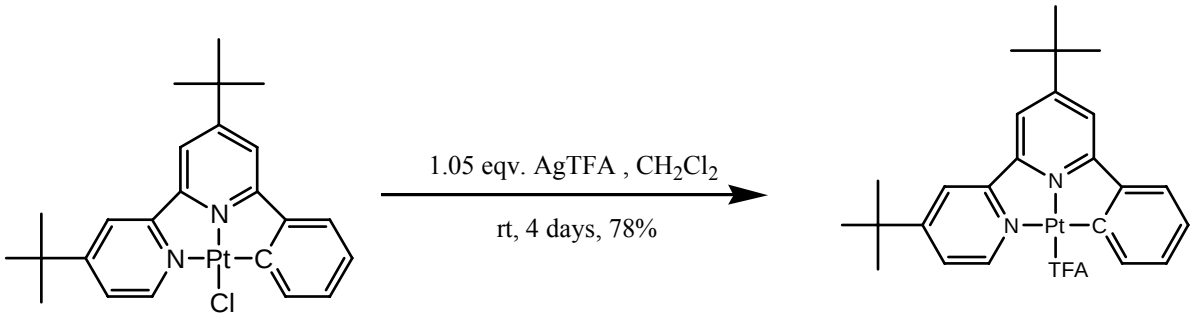
Complex **1** was prepared following a modified procedure reported by Lu and coworkers[1]. A suspension of K_2PtCl_4 (398mg, 0.958mmol) and 6-Phenyl-4, 4'-di-tert-butyl)-2,2'-bipyridine (300mg, 0.8708 mmol) in glacial acetic acid (10mL) were heated at 120°C for 3 days. The resulting orange suspension was allowed to cool to room temp, and then filtered over celite. The orange solid was washed with water (4 x 20mL), then ether (3 x 20mL), and then extracted with CH_2Cl_2. The product was then precipitated from CH_2Cl_2 with pentane. Yielding 412mg, 82.5% **^{1}H NMR** ($CDCl_3$, 400MHz) 8.82(d, 1H, ^3J = 5.8 J_{Pt-H} = 7.0, H-1), 7.75(d, 1H, ^4J = 1.8, H-4), 7.62(dd, 1H, ^3J = 7.6, ^4J = 1.4, J_{Pt-H} = 21.6, H-15), 7.49(dd, 1H, ^3J = 5.7 ^4J = 1.9, H-2), 7.46(d, 1H, ^4J = 1.6, H-7), 7.41(d, 1H, ^4J = 1.6, H-9), 7.26(dd, 1H, ^3J = 7.7, ^4J = 1.4, H-12), 7.13(dt, 1H, ^3J = 7.5, ^4J = 1.4, H-14), 7.00(dt, 1H, ^3J = 7.5, ^4J = 1.4, H-13), 1.43(s, 9H, -C(CH_3)$_3$), 1.41(s, 9H, -C(CH_3)$_3$). **^{13}C NMR** ($CDCl_3$, 100 MHz) 166.3(C-16, J_{PtC} = 53 Hz), 163.9(C-8), 163.1(C-3), 157.4(C-5, J_{PtC} = 26 Hz), 154.4(C-6, J_{PtC} =17 Hz), 148.7(C-1, J_{PtC} = 9 Hz), 147.1(C-10, J_{PtC} = 36Hz), 142.8(C-11), 135.3 (J_{PtC} = 25 Hz), 130.9 (J_{PtC} = 22 Hz), 124.4 (J_{PtC} = 5 Hz), 124.1 (J_{PtC} = 23 Hz), 123.9 (J_{PtC} = 13 Hz), 119.2 (J_{PtC} = 8 Hz), 115.8 (J_{PtC} = 24 Hz), 115.0 (J_{PtC} = 19 Hz), 36.1(-**C**(CH_3)$_3$), 35.9(-**C**(CH_3)$_3$), 30.7(-C(**C**H_3)$_3$), 30.6(-C(**C**H_3)$_3$)

Synthesis of Pt(4,4'-tBu_2(NNC))OC(O)CF_3 (3):

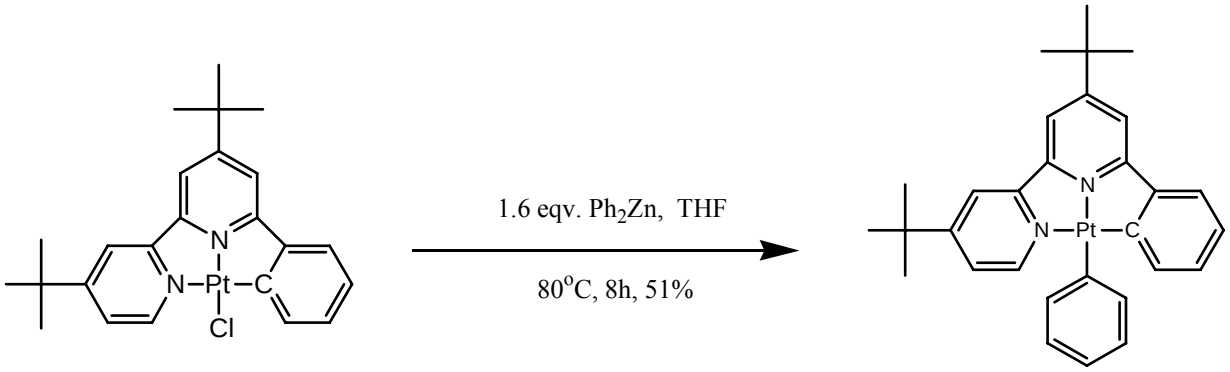


TFA=Trifluoroacetate

A solution of **1** (310.0mg, 0.5400 mmol) and silver trifluoroacetate (125.2 mg, 0.5670 mmol) in CH_2Cl_2 (30 mL) was stirred in the dark for 3 days. The resulting red solution was filtered over celite to remove the AgCl then evaporated to dryness. The solid was redissolved in a minimal amount of CH_2Cl_2, precipitated with pentane and filtered to give an orange-red solid in 77.93% yield. Elemental Calcd. for $C_{26}H_{27}F_3N_2O_2Pt$: C, 47.93; H, 4.18; F, 8.75; N, 4.30. Found C, 47.64; H, 4.27; F, 8.51; N, 4.22. **ESI-**

MS 674.1 $(M+Na)^+$, 652.2 $(M+H)^+$. **^{1}H NMR**($CDCl_3$, 400 MHz) 8.30 (d, 1H, ^3J = 6, H-1), 7.69 (d, 1H, ^4J = 2, H-4), 7.45 (dd, 1H, ^3J = 6, ^4J = 2, H-2), 7.30 (d, 1H, ^4J = 2, H-7), 7.19 (d, 1H, ^4J = 2, H-9), 7.02 (d, 1H, ^3J = 8, H-12), 6.94 (m, 1H, ^3J = 7, H-13), 6.93 (m, 2H, ^3J = 7, H-14), 6.62 (d, 1H, ^3J = 7 J_{Pt-H} ~ 38, H-15)[9], 1.40 (s, 9H, -$C(CH_3)_3$), 1.39 (s, 9H, -$C(CH_3)_3$). **^{13}C NMR**[10] ($CDCl_3$, 100 MHz,) 166.1(C-16), 164.1(C-3), 163.8(C-8), 162.3(**C**(O)CF_3, J_{C-F} = 36.8), 156.6(C-5), 155.1(C-6), 150.1(C-1), 146.9(C-11), 132.8(C-15), 130.5(C-14), 124.5(C-2), 124.4(C-13), 124.0(C-12), 119.6(C-4), 115.7(C(O)**CF_3**, J_{C-F} = 290.0), 115.4(C-9), 115.1(C-7), 35.8 (C-17), 35.6(C-21), 30.4(C-18,19,20), 30.3(C-22,23,24). **^{19}F NMR** ($CDCl_3$, 376 MHz) -73.8 (s).

Synthesis of Pt(4,4-tBu_2-[NNC])phenyl (4):



A solution of **1** (490.0 mg, 0.8536 mmol) and diphenyl zinc (300.0 mg, 1.366 mmol) in THF (30ml) was heated at 40°C for 2 h, then at 80°C for 8 h. The reaction was quenched with methanol, and the solvent was removed *in vacuo*. The residue was extracted with CH_2Cl_2 then filtered over celite. The

[9] We were unable to acurately measure a Pt-H satelites for H-15 due to a broad peak base.

[10] Only 15 of the 16 aromatic carbon resonances were observed. Ambiguity remained in the C-10 and C-11 assignments. Therefore, the assignment of C-11 was based off of **4**. Carbon-10 in **4** had a weak intensity in the ^{13}C NMR. As a result, it is assumed that the carbon resonance missing in the ^{13}C NMR for **3** is C-10.

product was obtained as an orange solid after separation on a Chromatotron from Harrison Research Company. The alumina used on the Chromatron was neutral aluminum oxide 60 GF_{254} (type E) for thin-layer chromatography. The aluminum oxide was obtained from EMD chemicals. The compound was eluted from the Chromatotron with a 25:75 mixture of CH_2Cl_2 : hexanes as the eluent. Other forms of alumina appeared to be too acidic as the compound could not be recovered from the column. Yield 51.29%. Elemental Calcd. for $C_{30}H_{32}N_2Pt$: C, 58.53; H, 5.24; N, 4.55. Found C, 58.06; H, 5.28; N, 4.58. **APCI-MS** 616.3 [$(M+H)^+$, 100%], 556.3 [$(M-Ph+H_2O)^+$, 15%], 538 [$(M-Ph)^+$, 5%]. **^{1}H NMR** ($CDCl_3$, 400 MHz) 8.54 (d, 1H, $^3J = 6$, $J_{PtH} = 9$, H-1), 7.87 (d, 1H, $^4J = 2$, H-4), 7.74 (dd, 2H, $^3J = 6$, $^4J = 1$, $J_{PtH} = 27.9$, ortho-phenyl (H-26,30), 7.67 (s, 1H, H-7), 7.63 (d, 1H, $^4J = 1.2$, H-9), 7.51 (dd, 1H, $^3J = 6$, $^4J = 1$, H-12), 7.44 (dd, 1H, $^3J = 4$, $^4J = 2$, H-2), 7.38 (d, 1H, $^3J = 8$, $J_{Pt-H} = 33.5$, H-15), 7.22 (t, 2H, $^3J = 7$, meta-phenyl(H-27,29)), 7.13 (dt, 1H, $^3J = 7$, $^4J = 1$, H-14), 7.07 (m, 2H, H-13, para-phenyl (H28)), 1.46 (s, 9H, $-C(CH_3)_3$), 1.42 (s, 9H, $-C(CH_3)_3$). **^{13}C NMR** ($CDCl_3$, 100 MHz) 164.3 (C-16, $J_{PtC} = 50$), 163.4(C-8), 163.1(C-3), 159.2 ($J_{PtC} = 11$, C-5), 155.3 (C-25), 153.6 ($J_{PtC} = 14$, C-6), 150.4 ($J_{PtC} = 12$, C-1), 148.0 ($J_{PtC} = 15$, C-10), 144.3 (C-11), 138.9 ($J_{PtC} = 10$, C-26,30), 137.5 ($J_{PtC} = 45$, C-15), 130.9 ($J_{PtC} = 39$, C-14), 127.4 ($J_{PtC} = 32$, C-27,29), 124.4 (C-12), 124.2 (C-2), 123.3 (C-13), 122.1 ($J_{PtC} = 5$, C-28), 119.3 ($J_{PtC} = 6$, C-4), 115.4 ($J_{PtC} = 11$, C-9), 114.3 ($J_{PtC} = 6$, C-7), 36.1 (C-17), 35.8 (C-21), 30.8 (C-18,19,20), 30.5 (C-22,23,24). *(The numbering of the molecule can be seen in figure 8 of the supporting information.)*

Stability test for 3: A Schlenck tube was charged with **3** (37.1 mg) in trifluoroacetic acid (1.5ml). The blue homogenous solution was then heated at 200^{o}C for 11h. The solvent was then removed under reduced pressure, and the blue solid washed with water and extracted into dichloromethane. After removal of solvents under reduced pressure, 45uL of a 0.3389M solution of 1,3,5-trimethoxybenzene in $CDCl_3$ was added then dissolved in $CDCl_3$. ^{1}H NMR analysis showed that **3** was the major species with minor amounts of what is believed to be the ion pair or solvento species was recovered with ~91% mass balance.

Reaction of Pt(4,4-tBu$_2$-[NNC])TFA (3) with tris(pentafluorophenyl)borane: In a J-young NMR tube **3** (16.9 mg, 0.0259 mmol) was dissolved in CD_2Cl_2. A NMR spectrum was obtained, followed by the addition of tris(pentafluorophenyl)borane (15.7 mg, 0.0306 mmol). Upon addition of the borane complex, the solution immediately changed color from a reddish-orange solution to an opaque dark blue solution. After addition of the borane, a NMR spectrum (Figure 1) was obtained verifying that **3** was completely reacted. There was primarily one species present in the NMR in roughly 48% mass balance (based on comparison to residual solvent). After allowing the J-young NMR tube to set overnight needle-like microcrystals could be seen on the on the walls of the NMR tube. Unfortunately none of these crystals diffracted.

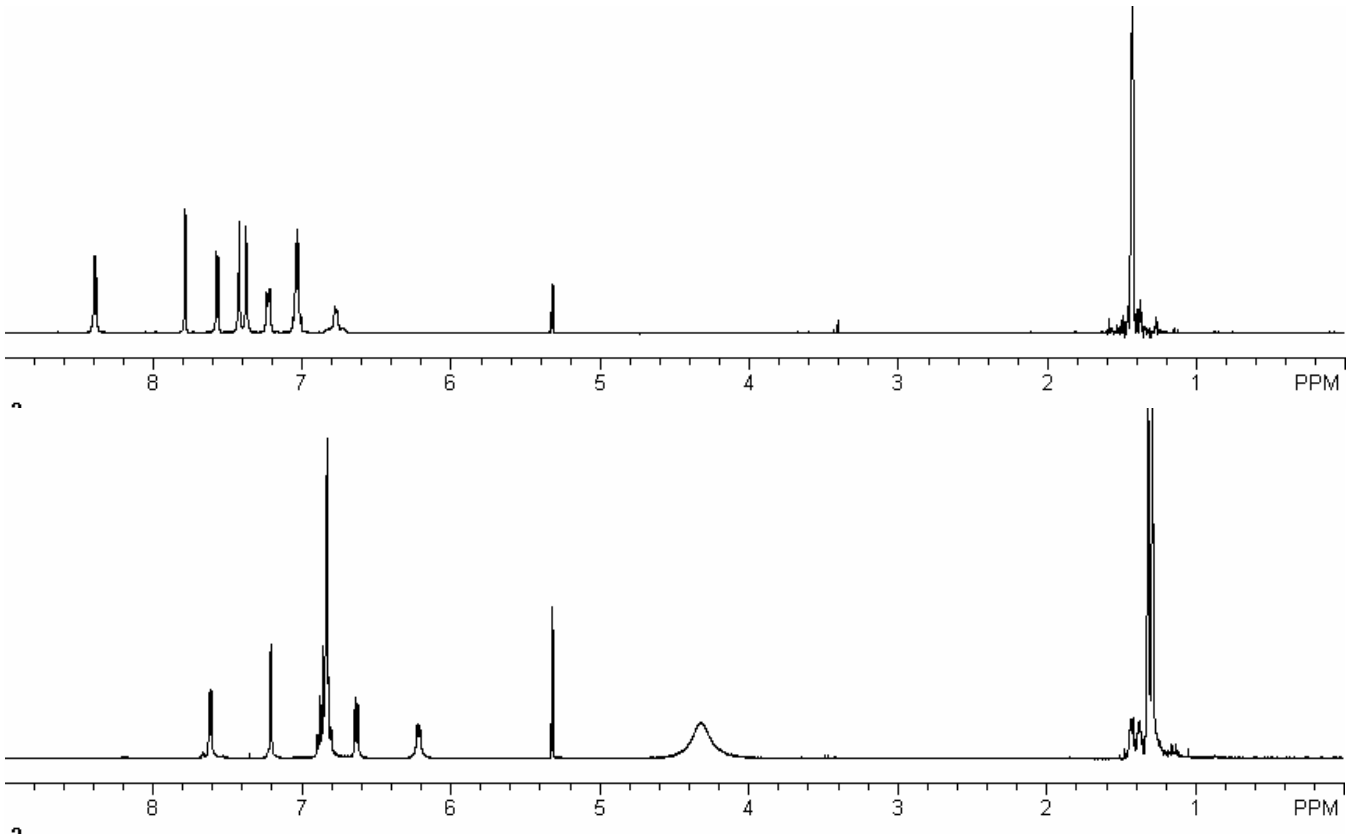


Figure 1. Top ^{1}H NMR of **3** inCD_2Cl_2. Bottom ^{1}H NMR after adding tris(pentafluorophenyl)borane.

General Procedure for H/D exchange studies with methane: In a typical reaction, approximately 6.5 to 9.0 mg of complex (**1** or **3)** was added to a 1.5 mL vial along with a Teflon stir bar, which was then placed into resealable, high pressure, 5ml, metal reactor. Under argon, 1.0 mL of solvent (sulfuric

acid-D_2 or trifluoroacetic acid-D_1) was added to the metal reactor. The reactor was then pressurized with 500 psi of methane while stirring. After pressurization, the reactor was stirred and heated to 180 or 200^oC for various times. A blank reaction was also prepared following the same procedure (1mL solvent, 500psi CH_4) but without any catalyst added to the reaction mixture. The blank was prepared to account for any H/D exchange between the acid solvent and methane. For analysis of H/D exchange with methane, the reactor was removed from the heating block and a vial with a septum (~2mL, flushed with argon prior to being placed under vacuum) was pressurized with the gas from the metal reactor. A 2.0-μL sample of the gas was taken from the vial and analyzed by GC-MS. Observation of methanol was performed by NMR analysis. A 10-μL amount of glacial acetic acid was added to the reaction mixture and the mixture was stirred to achieve homogeneity. This mixture was then placed in an NMR tube and analyzed using acetic acid as the internal standard.

Catalytic Reaction defined as 6.7 mg (0.012 mmols) of **1** in 1 mL of D_2SO_4 with 500 psi Methane. Blank reaction defined as 1mL D_2SO_4 and 500 psi methane. The reaction was carried out for 640 minutes.

Methane Isotopologs	Catalytic Reaction	Blank Reaction	"Blank Reaction" subtracted from "Catalytic Reaction" (corrected values)
CH4	81.90%	96.34%	85.56%
CH3D	9.05%	3.66%	5.39%
CH2D2	2.53%	0.00%	2.53%
CHD3	2.30%	0.00%	2.30%
CD4	4.22%	0.00%	4.22%

Table 1. Data obtained from the H/D exchange studies of **1** with CH_4 and Sulfuric acid-D_2.

Stoichiometric benzene activation studies: To a resealable Schlenk tube 14.2 mg (0.0218 mmol) of **3** and 5.0 μL (0.029 mmol) of Hunig's base were added to 1 mL of benzene. The tube was sealed and heated at to 180^oC for 6 hours. The benzene was then pumped off and the remaining yellow solid was taken up in $CDCl_3$. A NMR spectrum was obtained and only afforded complex **3**.

General Procedure for H/D exchange studies with benzene: In a typical reaction, approximately 6.5 to 9.0 mg of complex **3** or **4** and 0.25 mL of benzene-H_6 were added to a resealable Schlenk tube. Under argon, 1.0 mL of deuterated trifluoroacetic acid was added to the Schlenk tube. The tube was

sealed and heated at temperatures ranging from 160 to 190°C. A blank reaction was also prepared with 1.0 mL deuterated trifluoroacetic acid and 0.25 mL of benzene-H_6 under argon. At various times, the blank and catalyst tubes were removed from the oil bath and under argon a 0.2 μL sample was obtained from each Schlenk tube and analyzed by GC-MS. The tubes were then placed back into the oil bath for further heating.

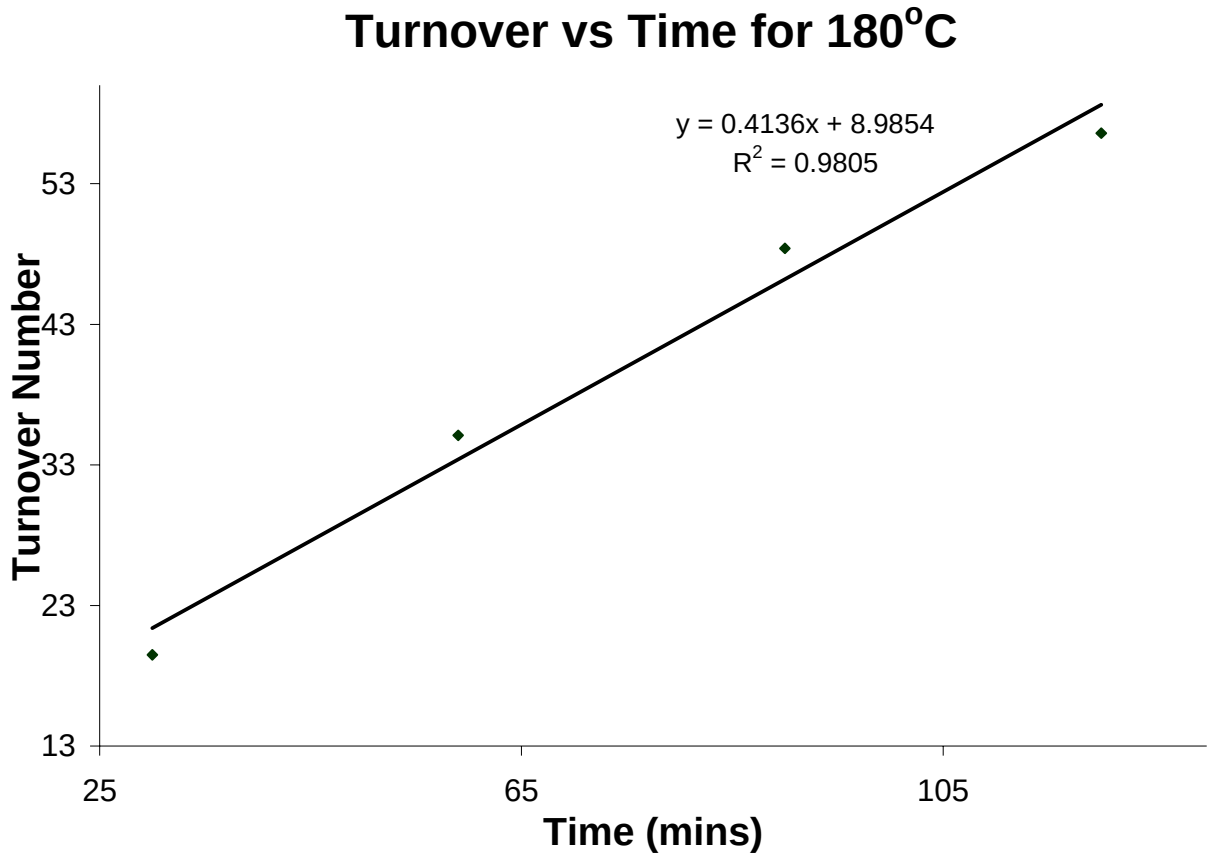


Figure 2. Turnover number vs. time plot for the H/D exchange reaction between benzene-H_6 and trifluoroacetic acid-D_1 with a 10.26mM concentration of complex **4** and 0.25mL benzene-H_6 and 1mL deuterated trifluoroacetic acid at 180°C. Correction for background H/D exchange has already been done prior to plotting the data.

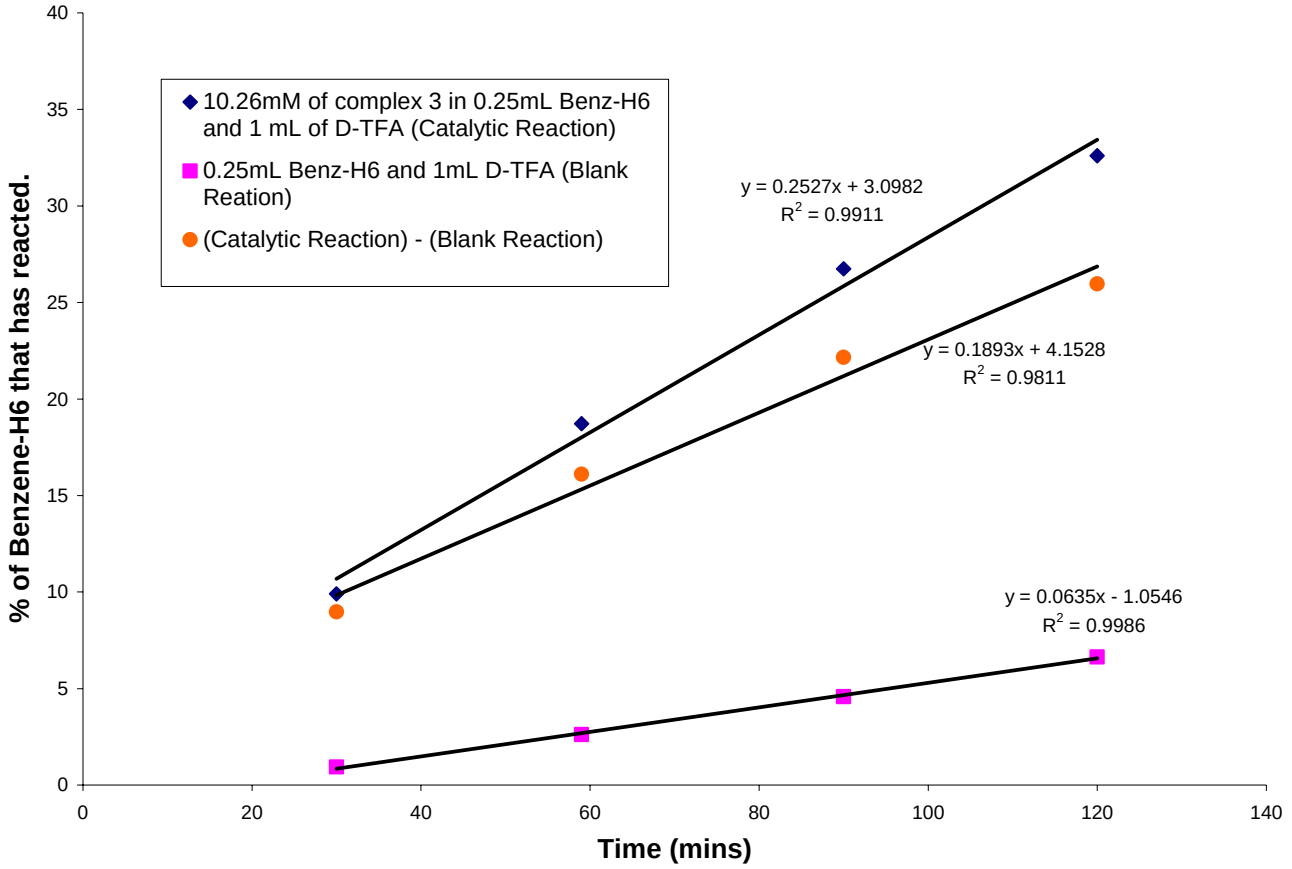


Figure 3. Plot of the %Benzene-H_6 that has reacted versus time in minutes for the "Catalytic reaction" and the "Blank reaction"

	% Deuterated Benzene Isotopologs from "Catalytic Reaction (uncorrected)"					
Time (mins)	% D1	% D2	% D3	% D4	% D5	% D6
30	9.42	0.44	0.02	0.00	0.00	0.01
59	17.01	1.59	0.09	0.01	0.01	0.01
90	23.14	3.33	0.27	0.03	0.01	0.01
120	27.08	4.92	0.51	0.06	0.02	0.01

	% Deuterated Benzene Isotopologs from "Blank Reaction"					
Time (mins)	% D1	% D2	% D3	% D4	% D5	% D6
30	0.85	0.06	0.00	0.00	0.00	0.01
59	2.50	0.09	0.01	0.00	0.00	0.00
90	4.34	0.17	0.04	0.01	0.00	0.01
120	6.19	0.33	0.07	0.02	0.01	0.01

Time (mins)	% Deuterated Benzene Isotopologs from ["Catalytic Rxn" – "Blank Rxn"] (corrected values)					
30	8.57	0.38	0.02	0.00	0.00	0.00
59	14.51	1.50	0.07	0.01	0.01	0.00
90	18.79	3.16	0.23	0.02	0.01	0.00
120	20.89	4.59	0.43	0.04	0.01	0.01

Table 2. Comparison of the % deuterated isotopologs of benzene with time for the "Catalytic reaction" and the "Blank reaction."

Reaction of 3 with benzene-H_6 and toluene-D_8: In a resealable Schlenk tube 10.1 mg (0.0164 mmol) of complex **3** was added to 0.5 mL of benzene-H_6 and 0.5 mL of toluene-D_8. The reaction was heated at 180^{o}C for 28 hours, after which a sample was taken and analyzed by GC-MS. After deconvolution, it was found that no H/D exchange was observed. A blank reaction consisting of only 0.5 mL benzene-H_6 and 0.5 mL of toluene-D_8 did not show any H/D exchange.

Analysis of H-D exchange: Catalytic H/D exchange reactions were quantified by monitoring the increase of deuterium into C_6H_6 by GC/MS analyses. This was achieved by deconvoluting the mass fragmentation pattern obtained from the MS analysis, using a program developed with Microsoft EXCEL. An important assumption made with this method is that there are no isotope effects on the fragmentation pattern for the various benzene isotopologs. Fortunately, because the parent ion of benzene is relatively stable towards fragmentation, it can be used reliably to quantify the exchange reactions. The mass range from 78 to 84 (for benzene) was examined for each reaction and compared to a control reaction where no metal catalyst was added. The program was calibrated with known mixtures of benzene isotopologs. The results obtained by this method are reliable to within 5%. Thus, analysis of a mixture of C_6H_6, C_6D_6 and $C_6H_5D_1$ prepared in a molar ratio of 40: 50: 10 resulted in a calculated ratio of 41.2(C_6H_6): 47.5(C_6D_6): 9.9($C_6H_5D_1$). Catalytic H/D exchange reactions were thus run for sufficient reaction times to be able to detect changes >5% exchange. Methane was analyzed in the same way as benzene using methane isotopologs. Turnover numbers for the catalytic reactions with methane and benzene were defined as TON =(moles of deuterated isotopologs of methane or benzene)/(moles of catalyst).

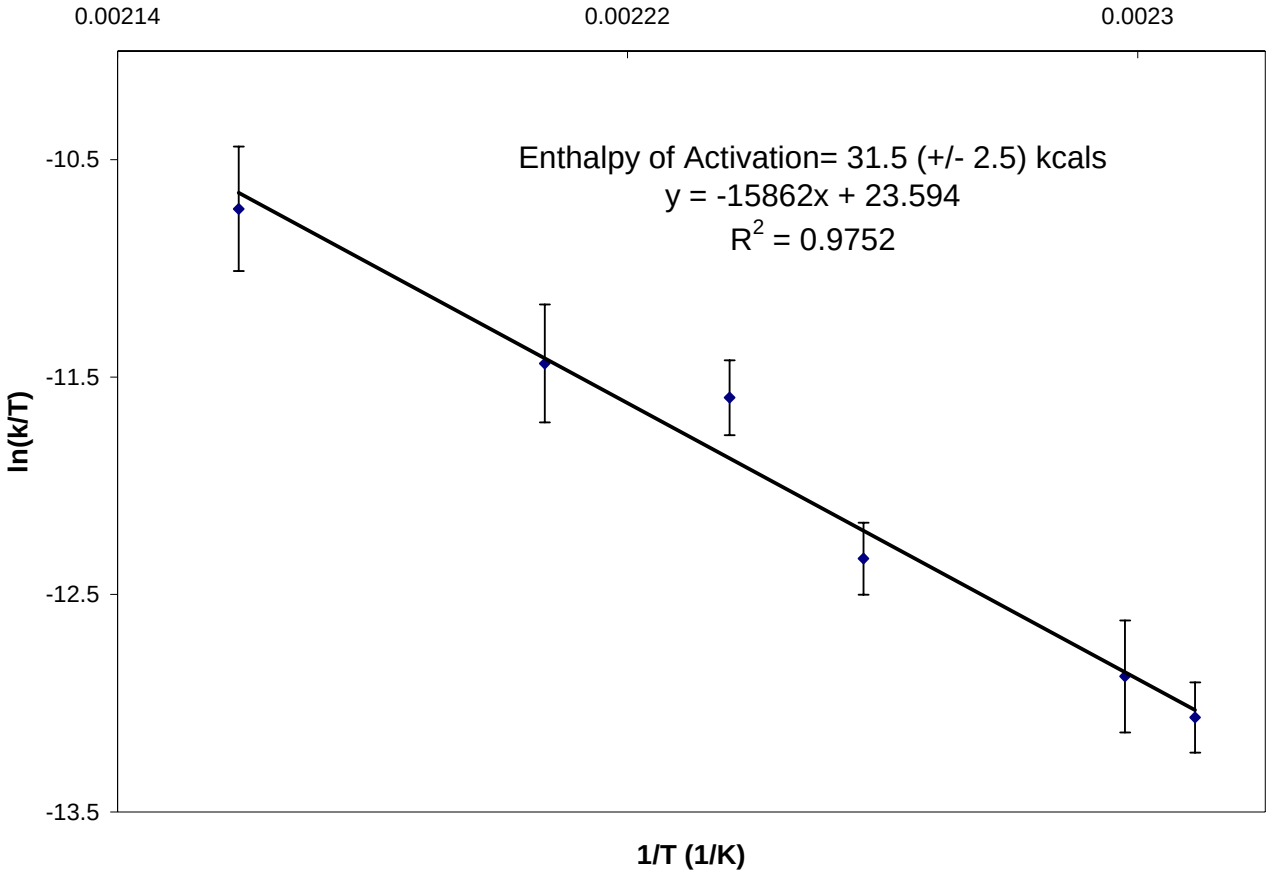


Figure 4. Eyring plot for Pt(NNC)TFA catalysis with benzene and trifluoroacetic acid-D_1.

Protonation Studies of Complex 4: In a NMR tube 8.0 mg (0.013 mmol) of **4** was dissolved in $CDCl_3$. A NMR spectrum was obtained for **4**. Then trifluoroacetic acid (3 μL) was added. After the addition of the acid a new NMR spectrum was obtained, Figure5. The NMR spectrum indicated the presence of free benzene and the formation of complex **3**.

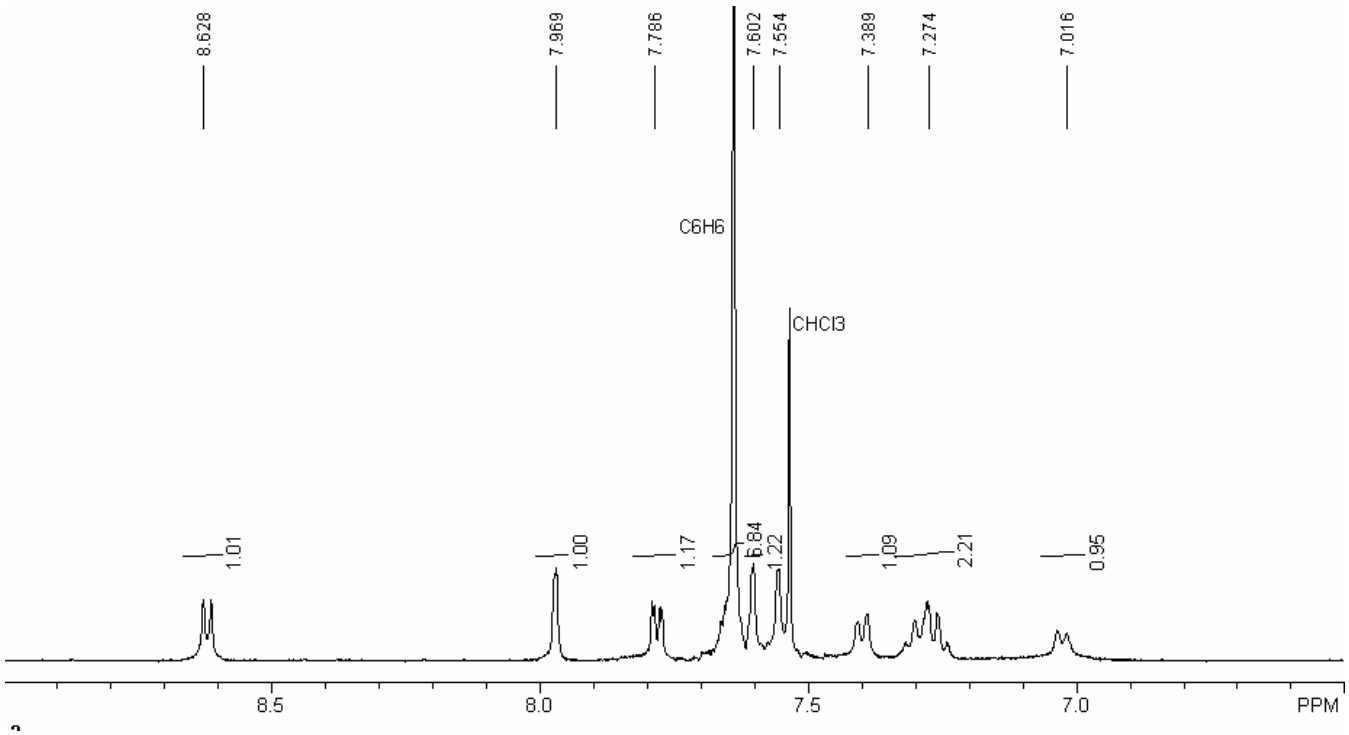
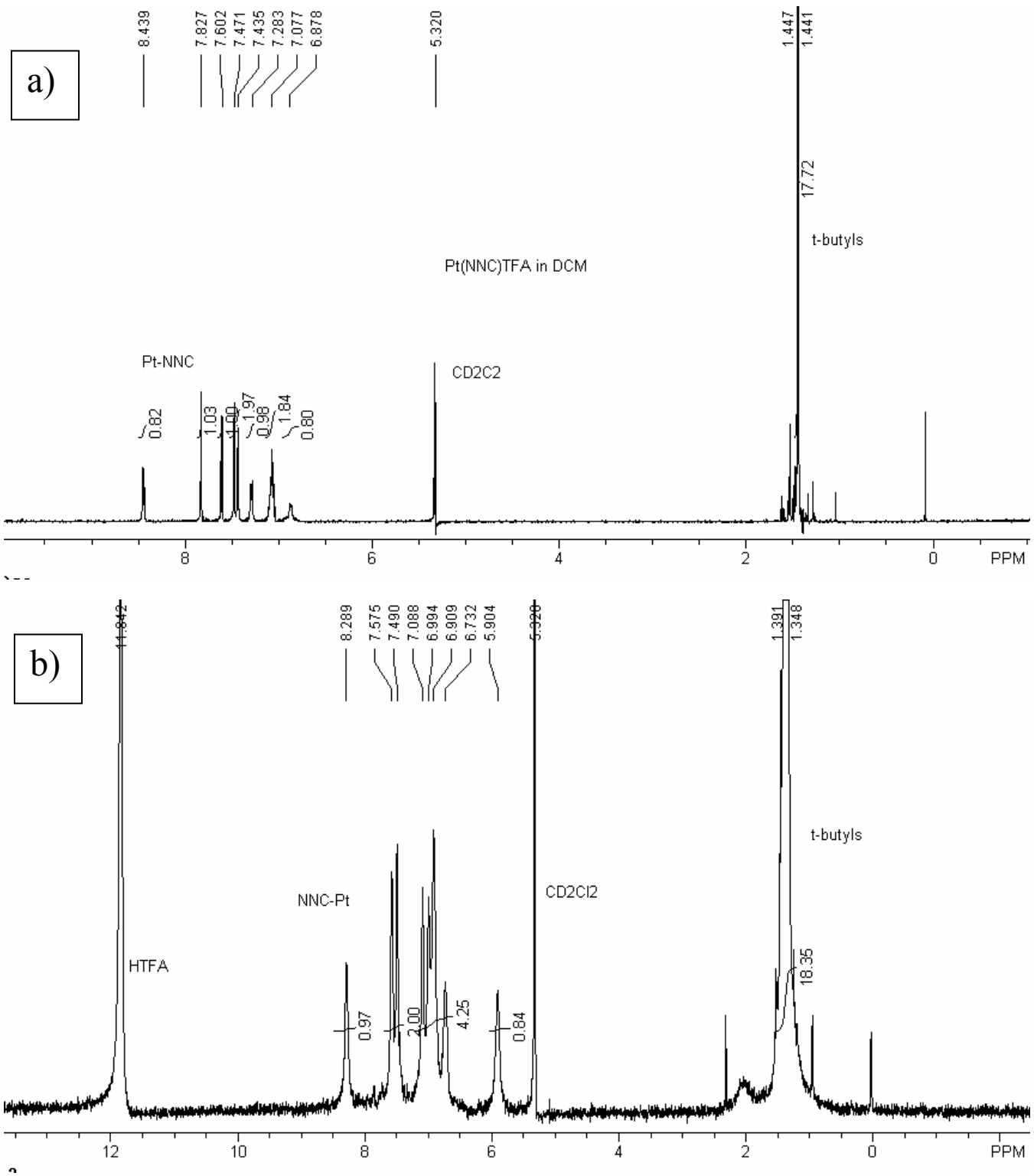


Figure 5. View of the aromatic region of the NMR spectrum of protonation of complex **4** with trifluoroacetic acid in deuterated chloroform.

Protonation Studies of Complex 3: In a J-young NMR tube 11.1mg (0.0170 mmol) of **3** was dissolved in approx. 0.75 mL of CD_2Cl_2. The NMR tube was then placed into the NMR probe and the probe was cooled to -70^{o}C. After obtaining an initial spectrum of **3**, the NMR tube was removed from the probe and approx 5 μL (0.065 mmols) of trifluoroacetic acid-H_1 was injected into the NMR tube. The solution rapidly changed color from an orange solution to a blue solution. The NMR tube was reinserted into the probe and an NMR (Figure 6) was obtained with a spectral window of -40 to 15 ppm. No hydride peak could be seen.


a)
8.439
7.827
7.602
7.471
7.435
7.283
7.077
6.878
5.320
1.447
1.441
17.72
t-butyls
Pt(NNC)TFA in DCM
Pt-NNC
CD2C2
0.82
1.03
1.00
1.97
0.98
1.84
0.80
8
6
4
2
0
PPM
b)
11.842
8.289
7.575
7.490
7.088
6.994
6.909
6.732
5.904
5.320
1.391
1.348
t-butyls
NNC-Pt
CD2Cl2
HTFA
18.35
0.97
2.00
4.25
0.84
12
10
8
6
4
2
0
PPM

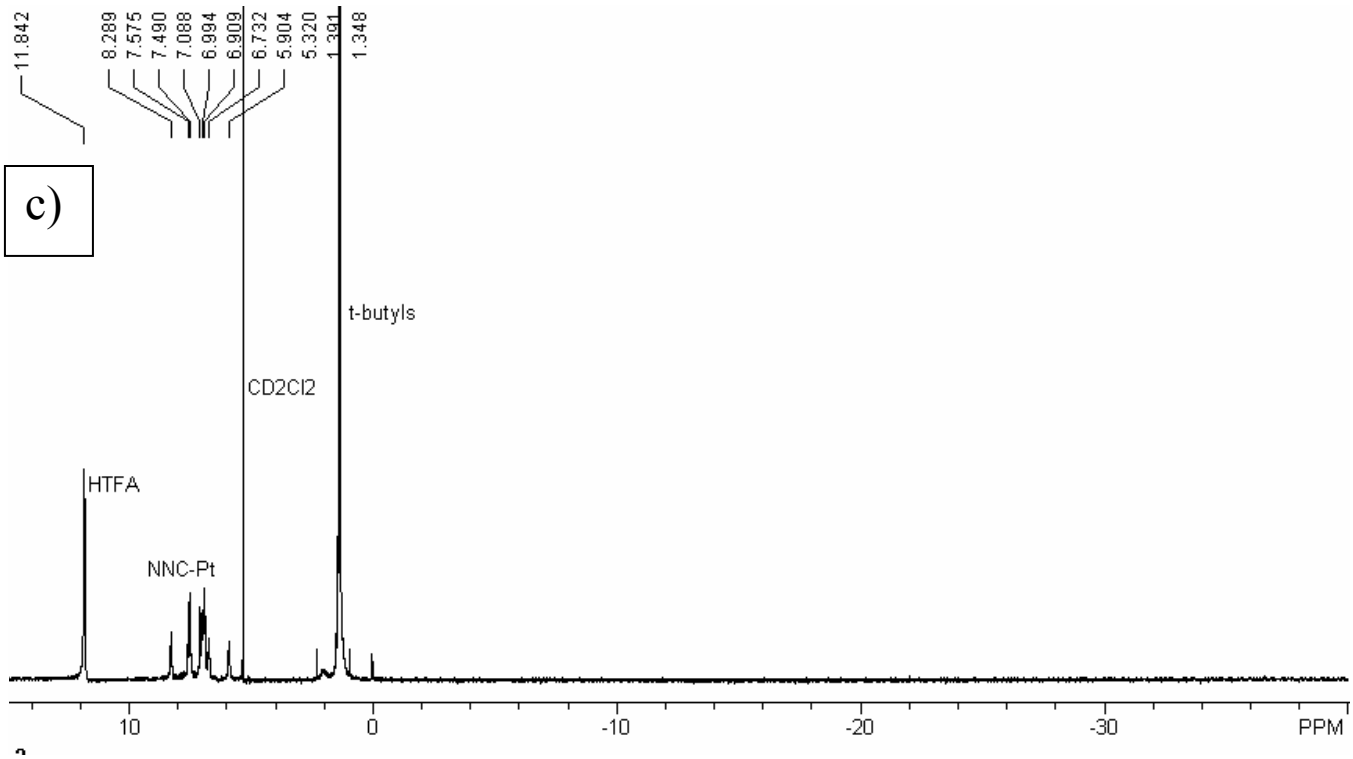


Figure 6. a) NMR spectrum of **3** in CD_2Cl_2. b) NMR spectrum of **3** with ~3.8 eq of HTFA in CD_2Cl_2. c) NMR spectrum of **3** with ~3.8 eq of HTFA in CD_2Cl_2 (full window).

Procedure for Catalyst recovery experiment: Inside a nitrogen filled box 10.8 mg of **4** and 0.25 mL of benzene-H_6 were added to a resealable Schlenk tube. Under argon, 1.0 mL of trifluoroacetic acid-H_1 was added to the Schlenk tube. The tube was sealed and heated to 190^{o}C for 100 minutes. The tube was then open under air and deionized water was added to the reaction mixture. The catalyst was then extracted with methylene chloride. The methylene chloride was then washed with water to remove any residual amounts of acid. The methylene chloride was then removed under vacuum and the sample was dissolved in $CDCl_3$. An internal standard was made containing 1,3,5-trimethoxybenzene. In a vial 3.9 mg of 1,3,5-trimethoxybenzene was added to 1.0 mL of $CDCl_3$. From this internal standard solution 100 µL (2.3×10^{-3} mmol) was added to the previously prepared NMR tube. With a relaxation delay of 60 secs integration obtained from the NMR spectra showed that complex **3**'s *ortho*-proton having an integration of 7.01 and the protons from 1,3,5-trimethoxybenzene were set as the reference with an integration of 3.00. Consequently, 1.6×10^{-2} mmol of catalyst was recovered resulting in a recovery yield of 92%. The fluorine NMR only showed one fluorine peak at -73.9 ppm.

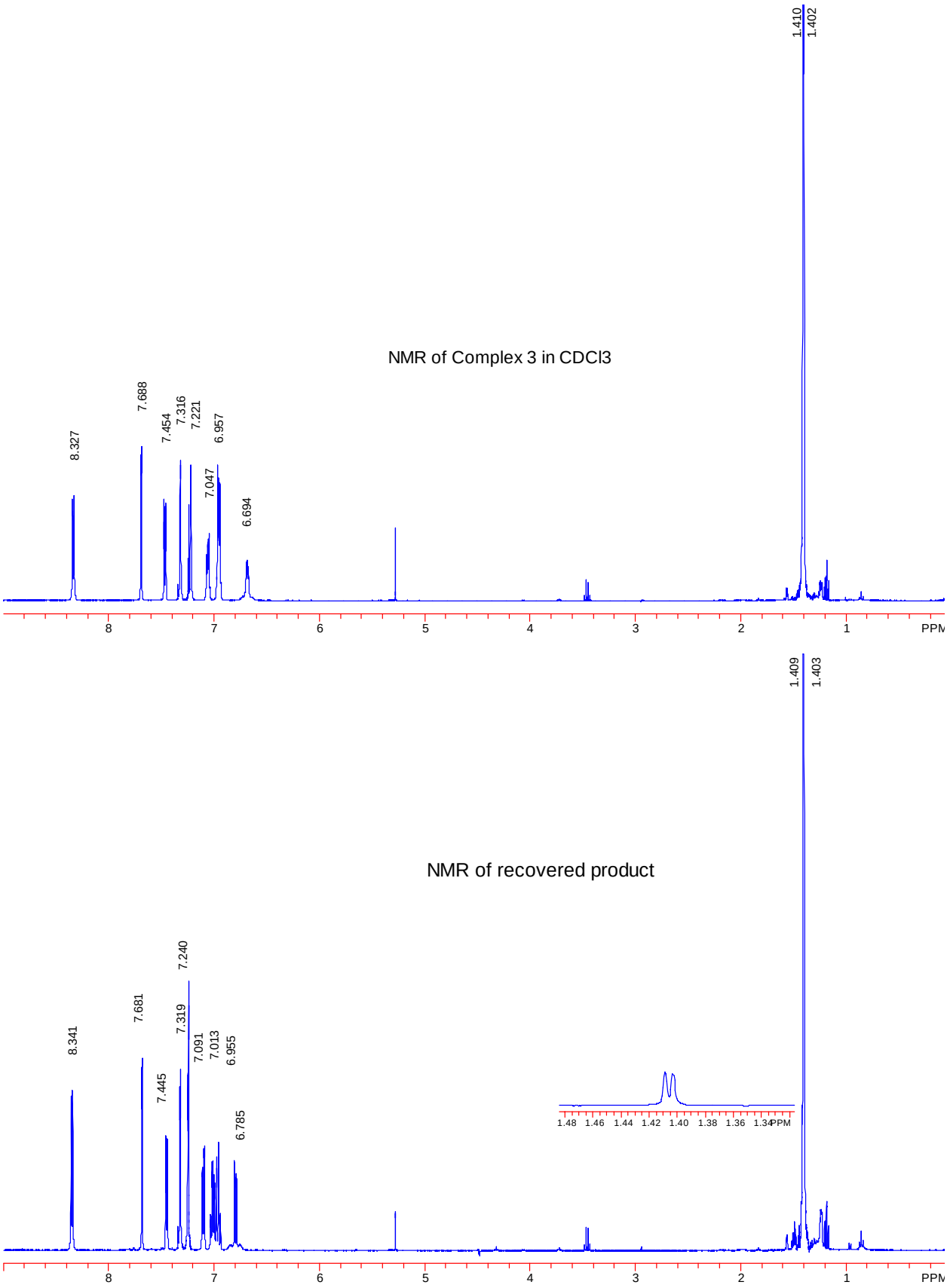


Figure 7. ^{1}H NMR of complex **3** in CDCl3 (top NMR). ^{1}H NMR of recovered product from "catalyst recovery experiment" (bottom NMR).

X-ray structure determination of Pt(4,4-tBu_2-[NNC])phenyl (4). Suitable crystals (amber) of **4** for x-ray analysis were grown from vapor diffusion of pentane into a benzene solution. Diffraction data was collected at 143K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The cell parameters were obtained from the least-squares refinement of the spots (collected 60 frames) using the SMART program. A hemisphere of data was collected up to a resolution of 0.75Å, and the intensity data was processed using the Saint Plus program. All calculations for the structure determination were carried out using the SHELXTL package (version 5.1).[11] Initial atomic positions were located by direct methods using XS, and the structure was refined by least-squares methods using SHELX with 11750 independent reflections and within the range of Φ1.39 to 25.68 (completeness 99.7%). Absorption corrections were applied by using SADABS.[12] Calculated hydrogen positions were input and refined in a riding manner along with the attached carbons. The thermal ellipsoid plot is shown in Figure 8. There are 2 molecules in the unit cell and it co-crystallized with a benzene solvent molecule. Crystal data and refinement parameters can be found in Table 3. Selected bond lengths and angles can be found in Table 5.

[11] Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

[12] Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33

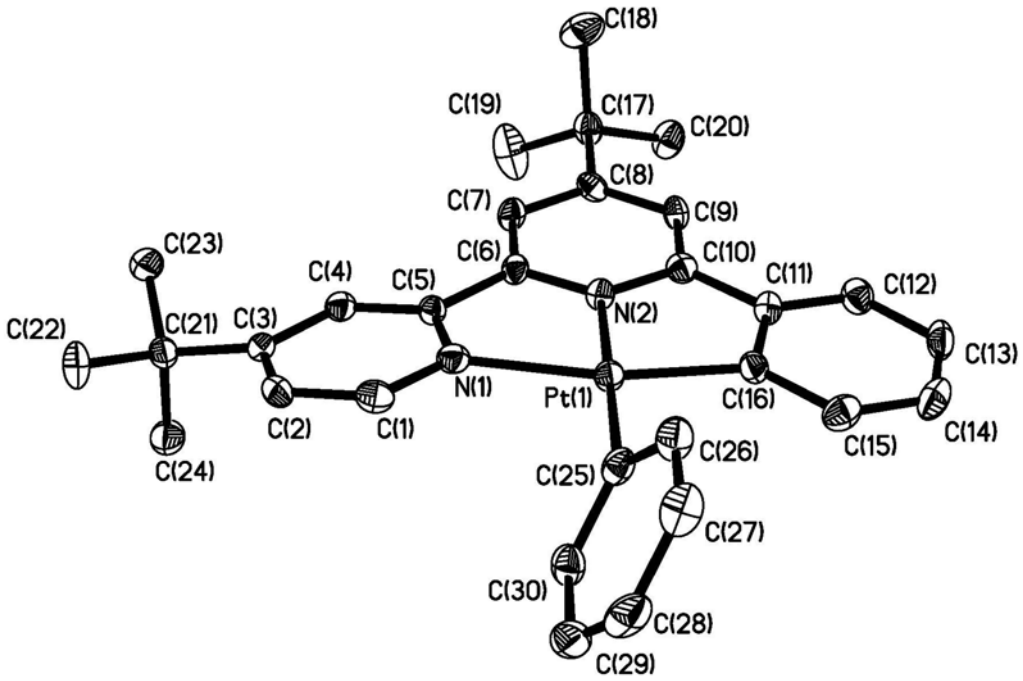


Figure 8. Thermal ellipsoid plot of **4** with 50% probability. Hydrogens and benzene co-solvent were removed for clarity.

Table 3. Crystal data and structure refinement for C36 H38 N2 Pt.

Identification code	steveptm	
Empirical formula	C36 H38 N2 Pt	
Formula weight	693.77	
Temperature	143(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 13.002(2) Å	α= 90°.
	b = 16.534(3) Å	β= 95.971(3)°.
	c = 13.345(2) Å	γ = 90°.
Volume	2853.3(8) $Å^3$	
Z	4	
Density (calculated)	1.615 Mg/m^3	
Absorption coefficient	4.945 mm^{-1}	
F(000)	1384	
Crystal size	0.17 x 0.12 x 0.03 mm^3	
Theta range for data collection	1.57 to 27.49°.	
Index ranges	-15<=h<=16, -19<=k<=21, -17<=l<=10	
Reflections collected	17411	
Independent reflections	6457 [R(int) = 0.0406]	
Completeness to theta = 27.49°	98.6 %	
Transmission factors min/max ratio:	0.739	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6457 / 0 / 358	
Goodness-of-fit on F^2	1.002	
Final R indices [I>2sigma(I)]	R1 = 0.0298, wR2 = 0.0638	
R indices (all data)	R1 = 0.0417, wR2 = 0.0677	
Largest diff. peak and hole	1.531 and -0.732 $e.Å^{-3}$	

Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for C36 H38 N2 Pt. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	6077(1)	1270(1)	5725(1)	17(1)
N(2)	6681(2)	186(2)	6124(2)	17(1)
N(1)	4763(2)	619(2)	6086(2)	19(1)
C(16)	7551(3)	1521(2)	5581(3)	19(1)
C(15)	8051(3)	2237(2)	5360(3)	24(1)
C(14)	9110(3)	2279(2)	5342(3)	28(1)
C(13)	9728(3)	1607(2)	5539(3)	25(1)
C(12)	9270(3)	879(2)	5761(3)	24(1)
C(11)	8210(3)	831(2)	5784(3)	18(1)
C(10)	7701(3)	80(2)	6069(3)	19(1)
C(9)	8133(3)	-679(2)	6283(3)	20(1)
C(8)	7521(3)	-1316(2)	6561(3)	19(1)
C(7)	6466(3)	-1171(2)	6619(3)	20(1)
C(6)	6067(3)	-409(2)	6408(3)	17(1)
C(5)	4982(3)	-138(2)	6450(3)	16(1)
C(4)	4251(3)	-605(2)	6874(3)	19(1)
C(3)	3243(3)	-322(2)	6894(3)	18(1)
C(2)	3019(3)	427(2)	6453(3)	21(1)
C(1)	3786(3)	870(2)	6070(3)	22(1)
C(17)	7976(3)	-2163(2)	6758(3)	22(1)
C(18)	7804(4)	-2643(2)	5764(4)	37(1)
C(19)	7452(4)	-2596(3)	7579(4)	45(1)
C(20)	9140(3)	-2132(2)	7098(3)	29(1)
C(21)	2449(3)	-782(2)	7454(3)	20(1)
C(22)	1347(3)	-547(3)	7058(3)	30(1)

C(23)	2568(3)	-1701(2)	7343(3)	26(1)
C(24)	2646(3)	-562(2)	8576(3)	28(1)
C(25)	5464(3)	2357(2)	5330(3)	21(1)
C(26)	5520(3)	2716(2)	4385(3)	26(1)
C(27)	5076(3)	3469(2)	4122(3)	29(1)
C(28)	4564(3)	3893(2)	4824(3)	30(1)
C(29)	4489(3)	3553(2)	5759(3)	28(1)
C(30)	4923(3)	2805(2)	5995(3)	24(1)
C(31)	7700(4)	1022(3)	8395(3)	35(1)
C(32)	8725(4)	1155(3)	8316(4)	40(1)
C(33)	9439(4)	567(3)	8595(4)	47(1)
C(34)	9130(4)	-170(3)	8953(4)	50(1)
C(35)	8088(4)	-307(3)	9032(3)	44(1)
C(36)	7378(4)	292(3)	8752(3)	35(1)

Table 5. Bond lengths [Å] and angles [°] for C36 H38 N2 Pt.

Pt(1)-C(16)	1.990(4)	C(17)-C(18)	1.543(6)
Pt(1)-N(2)	2.006(3)	C(21)-C(22)	1.525(5)
Pt(1)-C(25)	2.014(4)	C(21)-C(23)	1.536(5)
Pt(1)-N(1)	2.116(3)	C(21)-C(24)	1.537(5)
N(2)-C(6)	1.347(4)	C(25)-C(30)	1.400(5)
N(2)-C(10)	1.347(5)	C(25)-C(26)	1.403(5)
N(1)-C(1)	1.334(5)	C(26)-C(27)	1.402(5)
N(1)-C(5)	1.362(4)	C(27)-C(28)	1.393(6)
C(16)-C(15)	1.397(5)	C(28)-C(29)	1.382(6)
C(16)-C(11)	1.436(5)	C(29)-C(30)	1.382(5)
C(15)-C(14)	1.381(6)	C(31)-C(32)	1.367(6)
C(14)-C(13)	1.380(6)	C(31)-C(36)	1.378(6)
C(13)-C(12)	1.388(5)	C(32)-C(33)	1.369(7)
C(12)-C(11)	1.385(5)	C(33)-C(34)	1.383(7)
C(11)-C(10)	1.475(5)	C(34)-C(35)	1.388(7)
C(10)-C(9)	1.392(5)	C(35)-C(36)	1.380(6)
C(9)-C(8)	1.394(5)		
C(8)-C(7)	1.402(5)		
C(8)-C(17)	1.531(5)		
C(7)-C(6)	1.380(5)		
C(6)-C(5)	1.486(5)		
C(5)-C(4)	1.389(5)		
C(4)-C(3)	1.395(5)		
C(3)-C(2)	1.390(5)		
C(3)-C(21)	1.537(5)		
C(2)-C(1)	1.377(5)		
C(17)-C(19)	1.527(6)		
C(17)-C(20)	1.535(5)		

C(16)-Pt(1)-N(2)	81.83(14)
C(16)-Pt(1)-C(25)	98.47(15)
N(2)-Pt(1)-C(25)	179.65(15)
C(16)-Pt(1)-N(1)	159.50(13)
N(2)-Pt(1)-N(1)	77.80(12)
C(25)-Pt(1)-N(1)	101.89(13)
C(6)-N(2)-C(10)	122.4(3)
C(6)-N(2)-Pt(1)	120.0(2)
C(10)-N(2)-Pt(1)	117.5(2)
C(1)-N(1)-C(5)	117.1(3)
C(1)-N(1)-Pt(1)	128.9(2)
C(5)-N(1)-Pt(1)	113.9(2)
C(15)-C(16)-C(11)	115.6(3)
C(15)-C(16)-Pt(1)	132.2(3)
C(11)-C(16)-Pt(1)	112.1(3)
C(14)-C(15)-C(16)	122.2(4)
C(13)-C(14)-C(15)	121.1(4)
C(14)-C(13)-C(12)	119.0(4)
C(11)-C(12)-C(13)	120.3(4)
C(12)-C(11)-C(16)	121.7(3)
C(12)-C(11)-C(10)	121.9(3)
C(16)-C(11)-C(10)	116.3(3)
N(2)-C(10)-C(9)	119.0(3)
N(2)-C(10)-C(11)	112.0(3)
C(9)-C(10)-C(11)	129.0(3)
C(10)-C(9)-C(8)	120.4(3)
C(9)-C(8)-C(7)	118.3(3)
C(9)-C(8)-C(17)	121.0(3)
C(7)-C(8)-C(17)	120.6(3)
C(6)-C(7)-C(8)	119.7(3)

N(2)-C(6)-C(7)	120.2(3)
N(2)-C(6)-C(5)	112.5(3)
C(7)-C(6)-C(5)	127.3(3)
N(1)-C(5)-C(4)	121.9(3)
N(1)-C(5)-C(6)	115.3(3)
C(4)-C(5)-C(6)	122.7(3)
C(5)-C(4)-C(3)	120.4(3)
C(2)-C(3)-C(4)	116.5(3)
C(2)-C(3)-C(21)	121.7(3)
C(4)-C(3)-C(21)	121.6(3)
C(1)-C(2)-C(3)	120.2(3)
N(1)-C(1)-C(2)	123.6(3)
C(19)-C(17)-C(8)	111.0(3)
C(19)-C(17)-C(20)	107.6(3)
C(8)-C(17)-C(20)	111.8(3)
C(19)-C(17)-C(18)	109.9(4)
C(8)-C(17)-C(18)	107.7(3)
C(20)-C(17)-C(18)	108.7(3)
C(22)-C(21)-C(23)	108.6(3)
C(22)-C(21)-C(3)	111.1(3)
C(23)-C(21)-C(3)	111.4(3)
C(22)-C(21)-C(24)	109.4(3)
C(23)-C(21)-C(24)	108.7(3)
C(3)-C(21)-C(24)	107.7(3)
C(30)-C(25)-C(26)	115.0(3)
C(30)-C(25)-Pt(1)	121.2(3)
C(26)-C(25)-Pt(1)	123.9(3)
C(27)-C(26)-C(25)	122.9(4)
C(28)-C(27)-C(26)	119.5(4)
C(29)-C(28)-C(27)	119.1(4)

C(30)-C(29)-C(28)	120.3(4)
C(29)-C(30)-C(25)	123.3(4)
C(32)-C(31)-C(36)	120.1(4)
C(31)-C(32)-C(33)	120.3(5)
C(32)-C(33)-C(34)	120.4(5)
C(33)-C(34)-C(35)	119.4(5)
C(36)-C(35)-C(34)	119.6(5)
C(31)-C(36)-C(35)	120.2(5)

Symmetry transformations used to generate equivalent atoms:

Table 6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for C36 H38 N2 Pt. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pt(1)	16(1)	15(1)	20(1)	1(1)	3(1)	0(1)
N(2)	15(2)	17(2)	18(2)	2(1)	0(1)	1(1)
N(1)	20(2)	16(2)	21(2)	-2(1)	2(1)	2(1)
C(16)	17(2)	22(2)	17(2)	-1(2)	4(2)	-2(1)
C(15)	31(2)	18(2)	24(2)	3(2)	1(2)	-1(2)
C(14)	31(2)	23(2)	31(2)	4(2)	2(2)	-11(2)
C(13)	17(2)	35(2)	24(2)	-1(2)	4(2)	-9(2)
C(12)	19(2)	29(2)	22(2)	0(2)	1(2)	0(2)
C(11)	16(2)	20(2)	18(2)	2(2)	2(2)	-2(1)
C(10)	19(2)	23(2)	15(2)	-1(2)	0(2)	0(2)
C(9)	12(2)	24(2)	23(2)	4(2)	3(2)	1(1)
C(8)	21(2)	21(2)	16(2)	2(2)	4(2)	4(2)
C(7)	20(2)	15(2)	25(2)	5(2)	4(2)	-2(1)
C(6)	14(2)	20(2)	16(2)	0(2)	0(1)	-2(1)
C(5)	13(2)	19(2)	17(2)	-1(2)	1(1)	0(1)
C(4)	19(2)	17(2)	22(2)	-2(2)	2(2)	1(1)
C(3)	15(2)	20(2)	18(2)	-5(2)	2(2)	-3(1)
C(2)	17(2)	20(2)	26(2)	-2(2)	5(2)	3(1)
C(1)	24(2)	16(2)	24(2)	1(2)	2(2)	5(2)
C(17)	17(2)	21(2)	29(2)	4(2)	3(2)	3(2)
C(18)	41(3)	24(2)	46(3)	-8(2)	-3(2)	2(2)
C(19)	31(3)	39(3)	66(4)	31(3)	17(2)	14(2)
C(20)	20(2)	26(2)	41(3)	3(2)	-2(2)	2(2)
C(21)	16(2)	25(2)	19(2)	-2(2)	2(2)	-1(2)
C(22)	14(2)	38(2)	38(3)	5(2)	4(2)	-4(2)

C(23)	28(2)	23(2)	28(2)	-3(2)	7(2)	-5(2)
C(24)	28(2)	34(2)	23(2)	-5(2)	4(2)	-6(2)
C(25)	15(2)	19(2)	28(2)	1(2)	-2(2)	-1(1)
C(26)	22(2)	24(2)	31(2)	3(2)	2(2)	-1(2)
C(27)	25(2)	28(2)	33(3)	10(2)	-5(2)	-1(2)
C(28)	28(2)	13(2)	47(3)	2(2)	-4(2)	3(2)
C(29)	20(2)	24(2)	39(3)	-6(2)	2(2)	4(2)
C(30)	16(2)	26(2)	28(2)	3(2)	1(2)	0(2)
C(31)	42(3)	30(2)	33(3)	-3(2)	5(2)	2(2)
C(32)	44(3)	39(3)	38(3)	-9(2)	14(2)	-13(2)
C(33)	26(3)	60(3)	54(3)	-21(3)	3(2)	-1(2)
C(34)	50(3)	54(3)	42(3)	-17(3)	-15(3)	18(3)
C(35)	61(4)	37(3)	32(3)	-5(2)	1(2)	-5(2)
C(36)	35(3)	40(3)	30(3)	-6(2)	10(2)	-4(2)

Table 7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)

for C36 H38 N2 Pt.

	x	y	z	U(eq)		x	y	z	U(eq)
H(15)	7649	2711	5217	29	H(24B)	3335	-749	8844	42
H(14)	9419	2780	5192	34	H(24C)	2123	-821	8946	42
H(13)	10455	1642	5522	30	H(26)	5876	2438	3903	31
H(12)	9686	412	5898	28	H(27)	5123	3688	3471	35
H(9)	8850	-763	6239	24	H(28)	4271	4409	4661	36
H(7)	6029	-1595	6801	24	H(29)	4137	3834	6243	33
H(4)	4440	-1119	7153	23	H(30)	4852	2584	6641	28
H(2)	2335	635	6415	25	H(31)	7208	1433	8203	42
H(1)	3610	1382	5779	26	H(32)	8944	1658	8067	48
H(18A)	7062	-2670	5542	56	H(33)	10151	665	8542	56
H(18B)	8078	-3192	5871	56	H(34)	9626	-578	9144	60
H(18C)	8163	-2372	5247	56	H(35)	7866	-810	9276	53
H(19A)	7507	-2262	8190	67	H(36)	6664	202	8805	41
H(19B)	7793	-3117	7729	67	H(24A)	2605	27	8653	42
H(19C)	6721	-2686	7346	67					
H(20A)	9508	-1929	6545	44					
H(20B)	9388	-2677	7285	44					
H(20C)	9266	-1772	7681	44					
H(22A)	1235	-656	6333	45					
H(22B)	1242	30	7180	45					
H(22C)	857	-864	7407	45					
H(23A)	2026	-1977	7672	39					
H(23B)	3248	-1869	7661	39					
H(23C)	2505	-1844	6627	39					

Heterolytic CH Activation with a Cyclometalated Platinum (II) 6-Phenyl-4,4'-di-tert-butyl,-2,2-Bipyridine Complex.

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Supplemental Information

Experimental details: All theoretical calculations were performed with the B3LYP[2,3] density functional, in combination with the Jaguar 6.0[4,5] computational package. Platinum was described with the effective core potential of Hay and Wadt[6] while all other atoms used the 6-31G**[2] all electron basis set. The effects of diffuse functions were included with single point calculations. Solvation effects, in trifluoroacetic acid, (computed via single point corrections) were modeled implicitly with the PCM[7,8] model (ε = 8.55, solvent radius = 2.451).

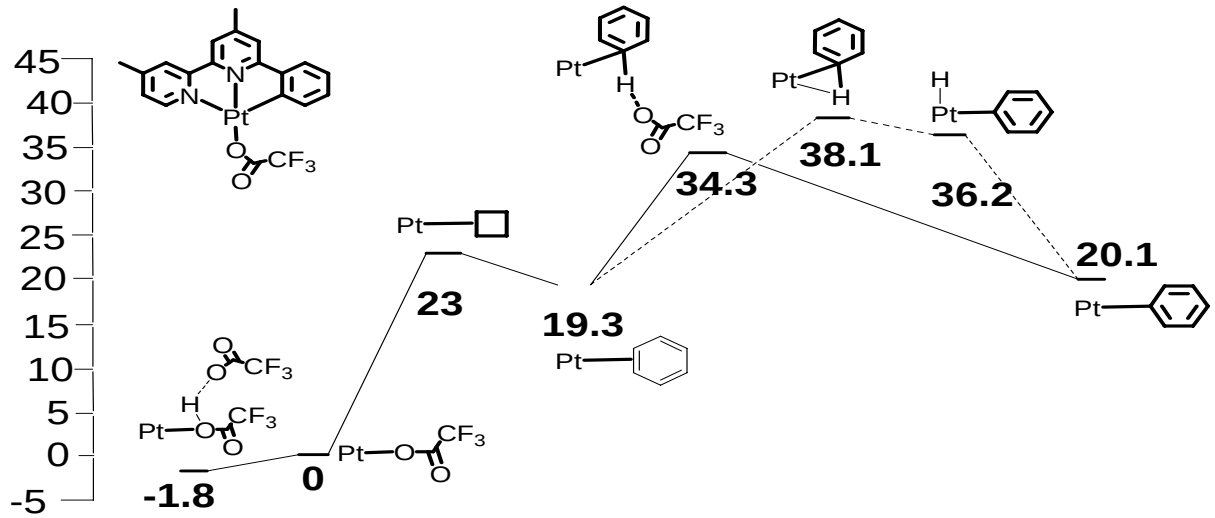

Figure 1. Energy diagram for $Pt(NN)TFA_2$ system.

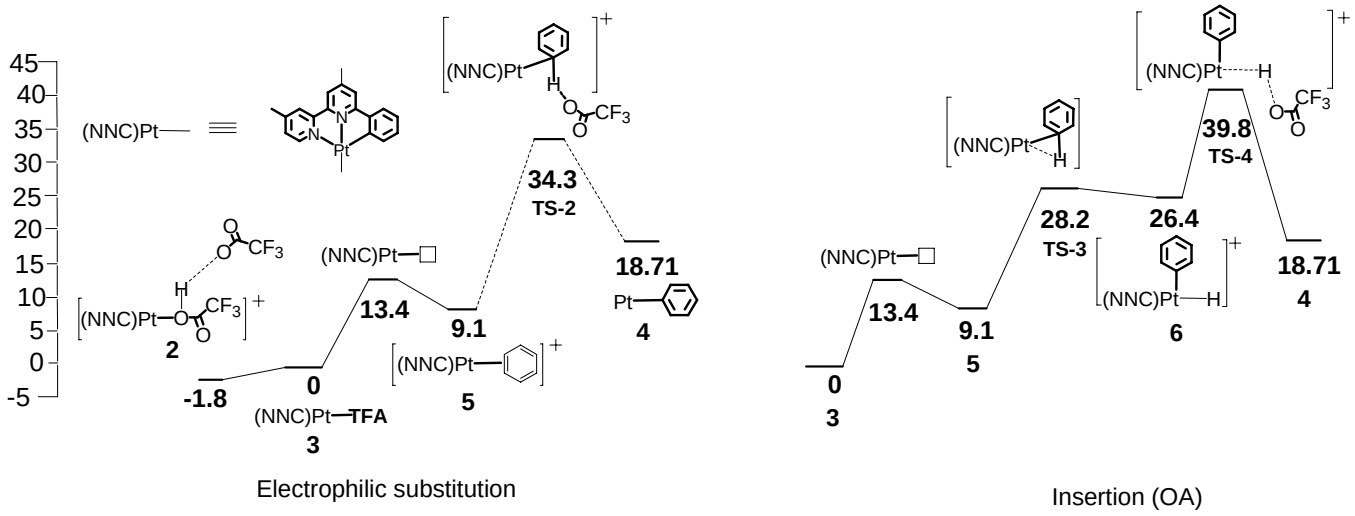

Figure 2. Energy diagram for Pt(NNC)TFA system.

Another possible mechanism for the H/D exchange reaction shown in Figure 2, is the concerted exchange of H with D for the intermediate Pt phenyl hydride complex, Pt(NNC)PhH, followed by the reverse reaction to form $C_6H_5D_1$. However, all attempts to find this barrier have been unsuccessful.

Cartesian coordinates (in Angstroms) and enthalpies (in kcal mol^{-1}) of key reactants, intermediates and products. The final two structures are for the reference Pt(NNC)-TFA and the ion-pair $[Pt(NNC)\text{-}HTFA]^+[TFA]^-$. These two species are the solvent optimized energetics and include energetics only.

C_6H_6
Enthalpy: -232.162842

C	0.7814125010	0.6386565305	-0.0000050474
C	2.1777188413	0.6386112900	0.0002959187
C	2.8758844836	1.8477410460	-0.0001081778
C	2.1778075027	3.0570121835	-0.0011641465
C	0.7815442188	3.0571069852	-0.0015720216
C	0.0833119042	1.8478908611	-0.0009497804
H	0.2381266915	-0.3023226145	0.0004337801
H	2.7208901183	-0.3024252404	0.0013833083
H	3.9624251163	1.8477506541	0.0002212558
H	2.7211829366	3.9979326053	-0.0014373535
H	0.2382470563	3.9980909384	-0.0022900858
H	-1.0032527033	1.8480124850	-0.0013266520

$(HTFA)_2$
Enthalpy: -1053.571232

H	-1.1262609738	-0.0302786312	-0.1340971766
H	-1.5644958490	-2.3104337595	-1.0136840286
O	-0.6827209088	0.5250287400	-0.8466170733
O	-2.0070784571	-2.8671184858	-0.3019275397
C	-2.1734135934	-2.1670059875	0.7879116837
C	-0.5189475987	-0.1746151300	-1.9372690935
O	-0.8383321049	-1.3399823429	-2.1282310708
O	-1.8568651531	-1.0006783406	0.9770373584
C	0.1632761930	0.6538108459	-3.0498266687
C	-2.8475126743	-2.9975101833	1.9037056704
F	0.3048830890	-0.0758415603	-4.1564054439
F	1.3745618396	1.0601261500	-2.6374633357
F	-0.5783065206	1.7364075296	-3.3329874875
F	-3.0594779852	-2.2450180096	2.9834313719
F	-2.0574986943	-4.0302506275	2.2396507890
F	-4.0224910087	-3.4803109576	1.4703759286

$TFA(HTFA)_2^-$
Enthalpy: -1579.942827

O	-0.5823326965	0.3056968689	1.7461976371
C	0.6412688369	0.2382181879	1.3364336762
O	1.1677888423	-0.6264141224	0.6543663943
C	1.5084674548	1.4392657909	1.8134320221
H	-1.1640967031	1.4730225707	2.4974049041
H	-1.4384533892	-0.8656993758	1.3088875000
O	-1.5630103516	2.2238748599	3.0907800036
O	-2.0974066217	-1.5856464984	0.9536493923
C	-2.0612935235	3.2094013640	2.3872257467
C	-2.1200624473	-2.6664892965	1.6892316607
O	-1.5261177287	-2.9157620345	2.7161090039
O	-2.1766336642	3.3171087566	1.1862458927
C	-2.5470603038	4.3382682358	3.3315825441
C	-3.0858400919	-3.7075596351	1.0660675249
F	-1.5314213613	4.8295987212	4.0732533506
F	-3.0751038281	5.3580282878	2.6356527304
F	-3.4936918958	3.8907732134	4.1854711267
F	-3.1332279537	-4.8288055756	1.8044141124
F	-2.7014117631	-4.0536273172	-0.1808981996
F	-4.3437552398	-3.2202847972	0.9820912801
F	2.7695925069	1.3693676267	1.3525376670
F	0.9911450195	2.6202114711	1.3961157083
F	1.5735433459	1.4901631642	3.1651308067

PtNNC—TFA
Enthalpy: -1449.653379

Pt	-0.9295790725	-0.7370320130	0.3056697820
C	1.0164583942	-0.3415773723	0.1840907201
C	1.2797957390	1.0452932825	-0.0095329497
C	2.0932486254	-1.2264325584	0.2683362638
C	2.5990053573	1.5104152732	-0.1182608558
C	3.4022949136	-0.7506326337	0.1578325920
H	1.8961316034	-2.2824116008	0.4223966945
C	3.6581310743	0.6118529930	-0.0357712053
H	2.8040993357	2.5673451660	-0.2676271637
H	4.2338629909	-1.4481699528	0.2227562245
H	4.6802341548	0.9690307180	-0.1212686169
C	-4.1501798770	-1.2678598245	0.4770435485
C	-3.4399355647	0.9206820890	0.1293091050
C	-5.4865568640	-0.8826271208	0.4091460095
H	-3.8399706336	-2.2923418596	0.6614345882
C	-4.7615679426	1.3614111613	0.0547117902
C	-5.8196878858	0.4567708206	0.1923251126
H	-6.2599272359	-1.6359278706	0.5244081557
H	-4.9754255018	2.4101085168	-0.1184974808
C	-2.2800959047	1.8328146943	-0.0136597535
C	0.0985911961	1.9070761949	-0.0847173339
C	-2.3506268637	3.2143782453	-0.1867374250
C	0.0519533949	3.2936331481	-0.2601380934
C	-1.1724040383	3.9638827235	-0.3115797601
H	-3.3117707578	3.7138800798	-0.2196870944
H	0.9786410029	3.8494853717	-0.3517495063
N	-3.1443670312	-0.3916147824	0.3333789955
N	-1.0752490309	1.2232779330	0.0397953714
O	-0.4866196646	-2.7349250805	0.5179599700
C	-1.2750294091	-3.6785276043	0.8948448664
C	-0.5267160787	-5.0383593721	0.9232844014
O	-2.4654770705	-3.6551021670	1.1805770132
F	-1.1734831277	-5.9410551383	1.6757759340
F	-0.4330609476	-5.5364385570	-0.3300508881
F	0.7262076378	-4.9183964915	1.4083606118
C	-7.2546299563	0.9140638878	0.1328718881
H	-7.6400386472	1.1029970172	1.1421556649
H	-7.3587714654	1.8403942019	-0.4388422091
H	-7.8947630760	0.1530584907	-0.3224274200
C	-1.2318868063	5.4564798551	-0.5215005114
H	-1.3262616373	5.6931278618	-1.5883616835
H	-2.0930356829	5.8977499331	-0.0111394737
H	-0.3264780144	5.9474195065	-0.1549015042

PtNNC--□
Enthalpy: -923.260680

Pt	-0.8329121904	-0.8480591510	0.0001673790
C	1.1229229182	-0.4264708101	0.0006939834
C	1.3602048385	0.9759824722	0.0117741548
C	2.2070777524	-1.2977283735	-0.0081254826
C	2.6694280343	1.4754876382	0.0123283215
C	3.5134899954	-0.7893337314	-0.0073955573
H	2.0547589789	-2.3745661135	-0.0160067167
C	3.7441268903	0.5885049279	0.0023486768
H	2.8578675834	2.5448824642	0.0200901678
H	4.3545511944	-1.4764793730	-0.0146496783
H	4.7600079300	0.9694256106	0.0022412748
C	-3.9982523031	-1.5541021732	-0.0078682857
C	-3.3687295255	0.6845649564	0.0093810872
C	-5.3480144517	-1.2195507572	-0.0146699681
H	-3.6800929649	-2.5916777470	-0.0146380225
C	-4.7036898188	1.0807796063	0.0017831639
C	-5.7307332805	0.1264143934	-0.0092595453
H	-6.0924187873	-2.0089208917	-0.0272464201
H	-4.9589082164	2.1339947439	0.0009866550
C	-2.2392821739	1.6452383966	0.0197365326
C	0.1598310088	1.8075806055	0.0218209604
C	-2.3446430061	3.0311296136	0.0389185918
C	0.0594924273	3.2019884626	0.0411643421
C	-1.1877303927	3.8308890346	0.0485062204
H	-3.3209349898	3.5003677446	0.0486068393
H	0.9671758615	3.7945380569	0.0525905958
N	-3.0244097167	-0.6329329169	0.0023457753
N	-1.0014863590	1.0903487740	0.0138203246
C	-7.1780058713	0.5381619061	0.0066024789
H	-7.5270059706	0.6505957873	1.0403031684
H	-7.3279938922	1.4968057201	-0.4969153303
H	-7.8114859063	-0.2111409048	-0.4740834435
C	-1.2988970088	5.3323932716	0.0423859860
H	-1.3569668975	5.7014491865	-0.9888390302
H	-2.1989261797	5.6694614467	0.5631659932
H	-0.4297327003	5.7996928158	0.5111315407

PtNNC—C_6H_6
Enthalpy: -1155.430066

Pt	-0.1091609160	-1.2416137830	0.0588458953
C	1.8415372227	-0.6949353267	0.1646281962
C	2.0003675366	0.7207870567	0.0799002872
C	2.9974270253	-1.4650193585	0.3022865557
C	3.2743059356	1.3078074803	0.1161914851
C	4.2645567713	-0.8703812047	0.3395204663
H	2.9476867131	-2.5469331902	0.3872429465
C	4.4082645304	0.5128852349	0.2420112739
H	3.3872272162	2.3855548235	0.0462087677
H	5.1438373709	-1.4980870518	0.4440495005
H	5.3930917301	0.9688452335	0.2672993688
C	-3.3265951094	-1.9224590650	-0.1334128018
C	-2.7029513889	0.3060763017	-0.1561330168
C	-4.6745883485	-1.5955803543	-0.2051600246
H	-3.0081447728	-2.9546139938	-0.0998937146
C	-4.0382599789	0.6946716667	-0.2267685940
C	-5.0632694417	-0.2551848045	-0.2431653499
H	-5.4130621773	-2.3894558500	-0.2301981086
H	-4.2929206584	1.7462006460	-0.2691804620
C	-1.5921424651	1.2842616731	-0.1417698036
C	0.7716422356	1.5036282447	-0.0327663639
C	-1.7382377647	2.6649114173	-0.2012364359
C	0.6497229728	2.8946559063	-0.0943134065
C	-0.6055242798	3.4938786534	-0.1783381061
H	-2.7236300102	3.1095784449	-0.2612746225
H	1.5400010340	3.5107428824	-0.0676828283
N	-2.3494188730	-1.0074504102	-0.1000674462
N	-0.3548330146	0.7460201234	-0.0607526129
C	-6.5117695886	0.1548313155	-0.2753711021
H	-6.8772674969	0.3307511426	0.7431414074
H	-6.6556164077	1.0806988429	-0.8382044258
H	-7.1382899494	-0.6233191468	-0.7178934128
C	-0.7556935665	4.9902173037	-0.2585377878
H	-0.9584622334	5.2973780074	-1.2908675545
H	-1.5922588273	5.3386339241	0.3541337923
H	0.1499346763	5.5033781236	0.0698921746
H	1.1431146757	-3.0627168687	1.5716572645
C	0.3418257428	-3.4131718745	0.9364826116
C	0.5003919337	-3.4864246590	-0.4741591555
C	-0.7574424861	-4.0785789280	1.5522767662
C	-0.4413254727	-4.2194431617	-1.2421509643
H	1.4319508144	-3.2020785518	-0.9520048809
C	-1.6384308885	-4.8148608236	0.7840449921
H	-0.8578597298	-4.0531342624	2.6349854367
C	-1.4781332998	-4.8834034220	-0.6210083028
H	-0.2987443750	-4.2971087418	-2.3155143337
H	-2.4492688170	-5.3599771339	1.2620424497
H	-2.1698009181	-5.4769587069	-1.2113749428

(PtNNC_Ph_H)‡ Oxidative Addition Transition State

Enthalpy: -1155.399624

Pt	-0.0550498719	0.2299606960	-0.0153670851
C	-0.0274019010	0.3335030113	2.0026662540
C	1.2782259289	0.1314661827	2.5415800798
C	-1.0930797386	0.5755680103	2.8636493208
C	1.4730539727	0.2079566163	3.9272055148
C	-0.8790914581	0.6441660242	4.2468474695
H	-2.0927483091	0.7180713422	2.4680904567
C	0.3979017532	0.4645476223	4.7775286251
H	2.4638675095	0.0697476636	4.3493263223
H	-1.7200122445	0.8335760170	4.9075943383
H	0.5569227457	0.5190989209	5.8494537466
C	0.1982152719	0.1256782592	-3.2740202440
C	2.1380511076	-0.3407655036	-2.0739966767
C	0.8299932312	-0.1316373031	-4.4848585974
H	-0.8394269775	0.4392535316	-3.2337487434
C	2.8204826994	-0.6146711904	-3.2573582648
C	2.1731543907	-0.5245830841	-4.4968668912
H	0.2724671274	-0.0249706815	-5.4100122778
H	3.8645181439	-0.9052531006	-3.2239641098
C	2.7904738004	-0.3968935680	-0.7370329674
C	2.3676375925	-0.1447197594	1.5928808093
C	4.1393921667	-0.6270741316	-0.4927967401
C	3.7192815123	-0.3707200240	1.8727187436
C	4.6186872201	-0.6168033166	0.8314983358
H	4.8309986190	-0.8017756601	-1.3084574855
H	4.0733927208	-0.3506510216	2.8969587692
N	0.8221953089	0.0130763364	-2.0929481932
N	1.9619577972	-0.1710951497	0.3025155566
C	2.8849724031	-0.8486802966	-5.7820814605
H	2.6577437657	-0.1096667867	-6.5560452483
H	3.9681259700	-0.8887677637	-5.6472626004
H	2.5571126878	-1.8243582347	-6.1603508284
C	6.0755630938	-0.8760811762	1.1085822675
H	6.3014650520	-1.9423152985	0.9879132316
H	6.7139382426	-0.3279579886	0.4090035994
H	6.3497573753	-0.5884364949	2.1255612706
H	-1.3112864704	-0.6208706806	0.2289297937
C	-1.8300420244	1.1762728113	-0.4630382259
C	-2.0390292127	2.4200921590	0.1491117783
C	-2.7301628370	0.7211940578	-1.4364659651
C	-3.1034133125	3.2267396008	-0.2608520455
H	-1.3717477407	2.7724615171	0.9288573994
C	-3.7986112962	1.5318600183	-1.8322061160
H	-2.6167052241	-0.2641437072	-1.8807480657
C	-3.9839776647	2.7856058251	-1.2495032091
H	-3.2444521717	4.1990326622	0.2028200924
H	-4.4924261983	1.1742086319	-2.5876765213
H	-4.8180151180	3.4107639207	-1.5535649223

PtNNC_H_Ph Oxidative Addition Intermediate
Enthalpy: -1155.402483

Pt	-0.8640027487	-0.7471504467	-0.2074670751
C	1.0972294716	-0.2729327344	-0.0623194915
C	1.2963300761	1.1030327498	0.2685668614
C	2.1976776259	-1.0953846771	-0.2825495325
C	2.6013250963	1.6039076392	0.3502687692
C	3.4944314623	-0.5709334480	-0.1975170473
H	2.0542328748	-2.1407897346	-0.5293231023
C	3.6964358463	0.7711654630	0.1199375003
H	2.7709182317	2.6500963772	0.5856706119
H	4.3457210604	-1.2205625954	-0.3787464156
H	4.7026471687	1.1721747381	0.1862620284
C	-4.0685871361	-1.2233458393	-0.5372391480
C	-3.4093588023	0.9335735643	0.0641502832
C	-5.4131195797	-0.8746102951	-0.4903864908
H	-3.7503345707	-2.2277081583	-0.7983973280
C	-4.7417472427	1.3356658327	0.1260094424
C	-5.7785791900	0.4328002105	-0.1517169796
H	-6.1661368907	-1.6220077587	-0.7188220376
H	-4.9856113180	2.3584238402	0.3894627696
C	-2.2725352859	1.8545355375	0.3518604606
C	0.1029251168	1.9483370807	0.4666557156
C	-2.3689718966	3.1983846002	0.7026300291
C	0.0446983676	3.2987423385	0.8265739749
C	-1.1956627264	3.9362487877	0.9481237052
H	-3.3330367814	3.6846013643	0.7934586664
H	0.9561102104	3.8543848282	1.0159295718
N	-3.0871078545	-0.3490365628	-0.2740788428
N	-1.0554153186	1.2894525170	0.2546882018
C	-7.2218977143	0.8483237195	-0.0651354676
H	-7.6139547059	0.6416688322	0.9381866192
H	-7.3458624414	1.9175951098	-0.2539665641
H	-7.8387557585	0.2937279627	-0.7769240866
C	-1.2821496521	5.3954834381	1.3114854773
H	-1.3922776827	6.0050879875	0.4064550887
H	-2.1482313164	5.5971516861	1.9479998677
H	-0.3831536103	5.7340590083	1.8312976617
H	-0.6735113705	-1.3372184426	1.1793090924
C	-0.7591660002	-2.6791233839	-0.8237886107
C	-0.1184411567	-3.7324257124	-0.1532124624
C	-1.3901073530	-2.9455703942	-2.0512229941
C	-0.1029628631	-5.0153804765	-0.7028997053
H	0.3787200333	-3.5590336971	0.7968970715
C	-1.3566988129	-4.2277544861	-2.6089341485
H	-1.8989609833	-2.1515385696	-2.5972906164
C	-0.7172627681	-5.2657475804	-1.9319217362
H	0.3931950856	-5.8216653464	-0.1700245723
H	-1.8321056336	-4.4103942777	-3.5686249905
H	-0.6984811675	-6.2641847856	-2.3583271025

(PtNNC_Ph_H_TFA)‡ External Reductive Elimination Transition State
Enthalpy: -1681.752839

Pt	-0.6336275786	0.3862521471	-0.3243974263

C	-0.4967839287	0.4655853887	1.6738477460
C	0.7813442269	0.0539054637	2.1550802412
C	-1.4652842679	0.8816432698	2.5826242489
C	1.0379571411	0.0781321845	3.5340215197
C	-1.1865440448	0.9049157742	3.9532894445
H	-2.4379354137	1.2020298283	2.2251183342
C	0.0608129685	0.5002265872	4.4316863939
H	2.0090878390	-0.2273097286	3.9124048556
H	-1.9511247184	1.2420466757	4.6485432120
H	0.2719325880	0.5173722234	5.4965863618
C	-0.4177501575	0.2634219803	-3.6298509652
C	1.5049156529	-0.3624568539	-2.4885950159
C	0.2164392597	0.1419560240	-4.8618408175
H	-1.4501091863	0.5856576437	-3.5527620892
C	2.1968961831	-0.5032266432	-3.6939962827
C	1.5577674933	-0.2510862306	-4.9117161867
H	-0.3336111073	0.3603331863	-5.7719199197
H	3.2413189211	-0.7943340314	-3.6899022368
C	2.1558843362	-0.5670967099	-1.1622221251
C	1.7975313097	-0.3508953467	1.1672477666
C	3.4672642449	-0.9952391572	-0.9563160060
C	3.1108987680	-0.7713582403	1.4182004294
C	3.9542955261	-1.1039475978	0.3561261902
H	4.1148671400	-1.2386500807	-1.7906519276
H	3.4788489959	-0.8350128093	2.4362923716
N	0.1999480725	0.0056229867	-2.4735710637
N	1.3794218853	-0.2806911441	-0.1099327213
C	2.2966323487	-0.3594989816	-6.2211110838
H	2.7202897115	0.6125187926	-6.5018681302
H	3.1224828032	-1.0734998142	-6.1591379990
H	1.6295517873	-0.6708149413	-7.0298250372
C	5.3601748402	-1.5910801674	0.6075281277
H	5.3991304811	-2.6868366733	0.5771261156
H	6.0532511144	-1.2182969926	-0.1525702400
H	5.7237315118	-1.2744633350	1.5884840800
H	-2.0955849200	0.9073727056	-0.3838565543
F	1.5326743012	4.4039289994	-2.4716118307
C	0.7728141575	4.5121082142	-1.3518766722
C	0.3176142874	3.1019356723	-0.8990507326
F	-0.2717303526	5.3090824658	-1.6493338038
F	1.5140614120	5.1417037856	-0.4243844933
O	-0.6334040395	2.6057002628	-1.5535399191
O	0.9541121057	2.5616199120	0.0267185864
C	-1.4739136322	-1.4606764755	-0.1582133114
C	-2.7573166661	-1.6337016138	0.3790761349
C	-0.7878428377	-2.5880803049	-0.6284497480
C	-3.3466512763	-2.8988229836	0.4231897445
H	-3.3060232355	-0.7806610319	0.7614781527
C	-1.3817315953	-3.8533434979	-0.5811095950
H	0.2101228926	-2.4965882454	-1.0413696376
C	-2.6637359112	-4.0159890734	-0.0578875044
H	-4.3466879085	-3.0056261005	0.8363496186

H	-0.8317696062	-4.7134412504	-0.9558859304
H	-3.1241999078	-4.9994824246	-0.0237027895

(PtNNC_Ph_H_TFA)‡ Electrophilic Substitution Transition State
Enthalpy: -1681.761535

Pt	-0.0803320707	-0.0580957142	0.0085091983
C	-0.0905614754	-0.1523870722	2.0259971862
C	1.2328452527	-0.1008160707	2.5690344621
C	-1.1429550655	-0.2781263977	2.9396878718
C	1.4573215081	-0.1472283146	3.9530924838
C	-0.9106457552	-0.3259363606	4.3177172726
H	-2.1618737946	-0.3396319737	2.5804409311
C	0.3858294117	-0.2551590884	4.8326259678
H	2.4692610804	-0.1019303961	4.3471587473
H	-1.7552250656	-0.4182720277	4.9963206435
H	0.5578894419	-0.2887892720	5.9042100180
C	0.0690340457	0.0791217423	-3.2234181238
C	2.0834841376	0.0581395434	-2.0656403158
C	0.7262523252	0.1515047097	-4.4461574377
H	-1.0105409337	0.1005937021	-3.1647668887
C	2.7968557229	0.1361549411	-3.2623870333
C	2.1229764219	0.1855433763	-4.4861340659
H	0.1416478231	0.1972437204	-5.3595975104
H	3.8804349121	0.1672084423	-3.2472412052
C	2.7426351805	0.0357447522	-0.7390142930
C	2.3251985916	-0.0221010029	1.6007445631
C	4.1164617727	0.0921642440	-0.5184207826
C	3.7017632171	0.0425362306	1.8498692031
C	4.6118632590	0.0982250674	0.7948266842
H	4.8050011935	0.1426151341	-1.3536483295
H	4.0592476582	0.0526654614	2.8733858457
N	0.7245374977	0.0209467613	-2.0556764145
N	1.8964392141	-0.0215894869	0.3139123046
C	-1.7491588964	3.0281262049	-1.3061134310
C	-1.1840948367	4.2155991867	-2.1356862670
O	-2.1255395498	3.2526804279	-0.1559429447
F	-1.3205103961	5.3972748475	-1.5141217123
F	0.1428173297	4.0327144842	-2.3684060237
F	-1.7841204410	4.3184178549	-3.3433462296
C	2.8672083044	0.3075250003	-5.7901418402
H	2.8486467834	1.3460219895	-6.1416803030
H	3.9139100227	0.0086825872	-5.6880676596
H	2.4056707963	-0.3067769394	-6.5691907359
C	6.0975533777	0.1503690469	1.0477599187
H	6.5603981602	-0.8204557636	0.8343466466
H	6.5831553255	0.8904875555	0.4038422029
H	6.3180258725	0.4037851483	2.0874514495
H	-1.8732494450	0.7374457846	-1.0384783263
O	-1.7075529724	1.9290585075	-1.9605303183
C	-2.2903629223	-0.1861782656	-0.3627124192
C	-2.5169103618	-1.4718130415	-0.9105450607
C	-3.2669495729	0.3410686585	0.5172969819
C	-3.6287879552	-2.2275219436	-0.5409962239
H	-1.8108890824	-1.8842788852	-1.6273841618
C	-4.3924084345	-0.3989002877	0.8630615056

H	-3.1334243510	1.3666112835	0.8533869375
C	-4.5630664622	-1.6897411912	0.3474290546
H	-3.7775983791	-3.2220250646	-0.9520679065
H	-5.1444727425	0.0242499104	1.5236120300
H	-5.4406668221	-2.2698269661	0.6223286141

PtNNC—Ph
Enthalpy:

Pt	-0.8090501019	-0.8959009455	-0.0230875720
C	1.1319195943	-0.4073507630	0.0502650431
C	1.3389049178	1.0131628424	0.1047034208
C	2.2725336520	-1.2205047958	0.0447413075
C	2.6338765291	1.5504331512	0.1581024296
C	3.5571632171	-0.6734040460	0.0979451973
H	2.1511332991	-2.2977955345	0.0004195760
C	3.7434375550	0.7107280682	0.1559313482
H	2.7812387037	2.6266485689	0.1997287250
H	4.4219743051	-1.3331495013	0.0925096884
H	4.7446305668	1.1301937775	0.1967709691
C	-3.9563592158	-1.5136838111	-0.1488342326
C	-3.3474395041	0.7337055290	-0.0711675839
C	-5.3088562551	-1.1931794554	-0.1850492817
H	-3.6090630795	-2.5424331945	-0.1717082134
C	-4.6906446864	1.1118303858	-0.1065682370
C	-5.7032581403	0.1488505696	-0.1607882239
H	-6.0462255437	-1.9887504973	-0.2337627337
H	-4.9542572418	2.1636339556	-0.0943676603
C	-2.2310787698	1.7150872571	-0.0054068556
C	0.1369967444	1.8632314813	0.0914948323
C	-2.3545191538	3.1043202433	0.0461153038
C	0.0519863688	3.2608430855	0.1458976512
C	-1.1958488686	3.8924413251	0.1206723278
H	-3.3291752882	3.5798754308	0.0348920363
H	0.9553337657	3.8579061551	0.2107564519
N	-2.9936381844	-0.5832412412	-0.0938645021
N	-1.0116219469	1.1526313935	0.0171566640
C	-7.1585436198	0.5411732713	-0.1679075572
H	-7.5503426748	0.5859207561	0.8556224180
H	-7.3078957850	1.5255826162	-0.6203368742
H	-7.7625926584	-0.1867992703	-0.7162335370
C	-1.2982878128	5.3981857403	0.1488359800
H	-1.2910714334	5.8060607973	-0.8694331977
H	-2.2257364863	5.7274410901	0.6266802404
H	-0.4577004965	5.8454796372	0.6865421888
C	-0.6574707532	-2.9181798569	-0.0318549706
C	-0.0557977650	-3.6450559312	1.0170779439
C	-1.2403445849	-3.6798115265	-1.0682275620
C	-0.0489469985	-5.0417619846	1.0384733539
H	0.4160423852	-3.1055077631	1.8347218195
C	-1.2279344169	-5.0782951036	-1.0581215823
H	-1.7030036428	-3.1698035766	-1.9119272050
C	-0.6346506988	-5.7680427244	-0.0005241686
H	0.4176883188	-5.5662312086	1.8699603526
H	-1.6790254024	-5.6291268722	-1.8813405061
H	-0.6252594213	-6.8550511552	0.0127357447

Solution Phase Structures and Energetics

PtNNC—TFA
Energy: -1449.993570

Pt	-0.9458752367	-0.7363717099	0.2711866523
C	1.0117239248	-0.3415342435	0.1898793665
C	1.2772370687	1.0477321954	0.0112250333
C	2.0912693438	-1.2229563831	0.2890229492
C	2.5971245116	1.5152292056	-0.0675380688
C	3.4054575705	-0.7471264125	0.2095968234
H	1.8990899709	-2.2818547305	0.4315147966
C	3.6597274311	0.6167751525	0.0312899442
H	2.8031104949	2.5737980438	-0.2041938314
H	4.2358826777	-1.4457314718	0.2882566768
H	4.6824359461	0.9787077196	-0.0285497418
C	-4.1734148403	-1.2626837511	0.4051527733
C	-3.4511392561	0.9301218506	0.1122720810
C	-5.5082360989	-0.8701967051	0.3708700963
H	-3.8816517493	-2.2958222990	0.5554798345
C	-4.7698469079	1.3808189119	0.0748912476
C	-5.8343831459	0.4800981296	0.2075612080
H	-6.2841245259	-1.6230396490	0.4768068279
H	-4.9785138696	2.4371392138	-0.0582992604
C	-2.2881209655	1.8399649574	-0.0210638571
C	0.0930422931	1.9133227592	-0.0746856903
C	-2.3538068405	3.2223506208	-0.1853792065
C	0.0526875672	3.2986510022	-0.2415700099
C	-1.1724883698	3.9712771987	-0.3002128320
H	-3.3141992716	3.7240723528	-0.2244758307
H	0.9805961084	3.8553914291	-0.3238181480
N	-3.1592522418	-0.3918098167	0.2769866098
N	-1.0812396420	1.2283433385	0.0323327006
O	-0.4990960840	-2.7629030807	0.4630962208
C	-1.2347300945	-3.6993090364	0.9336631241
C	-0.4752496928	-5.0537815366	0.9583140007
O	-2.4008757016	-3.6801924860	1.3185537842
F	-1.0106935114	-5.9000740013	1.8554319985
F	-0.5485378430	-5.6461660967	-0.2567411490
F	0.8303413922	-4.9083022716	1.2608191532
C	-7.2653417462	0.9512668881	0.2037136003
H	-7.6157192027	1.0983318560	1.2340339540
H	-7.3755707232	1.9037730988	-0.3232151202
H	-7.9239011002	0.2123841647	-0.2633182209
C	-1.2260868883	5.4632721628	-0.5070865605
H	-1.3361534361	5.6926196384	-1.5748623989
H	-2.0791618169	5.9070702537	0.0151293183
H	-0.3097232384	5.9468808222	-0.1568071638

[Pt(NNC)—HTFA]$^{+}$[TFA^{-}]
Energy: -1976.824934

Pt	-1.1897848122	-0.7840023153	0.3802734363
C	0.7915832237	-0.4971263030	0.4718824785
C	1.1392752653	0.8828198332	0.3582344614
C	1.8248718014	-1.4312030528	0.5815346441
C	2.4814426678	1.2883460704	0.3866349914
C	3.1629198076	-1.0181076900	0.6047298447
H	1.5934325022	-2.4887259491	0.6429028214
C	3.4940518910	0.3373830214	0.5147020975
H	2.7428457032	2.3400689732	0.3028060790
H	3.9511954093	-1.7621888702	0.6920041139
H	4.5339397619	0.6506961673	0.5362785667
C	-4.3990656886	-1.1864083510	-0.0219243447
C	-3.5605304918	0.9800374935	-0.1480827800
C	-5.6873724441	-0.7479911489	-0.3141984550
H	-4.1834383718	-2.2369088759	0.1298057876
C	-4.8283293218	1.4773561665	-0.4456033406
C	-5.9269604359	0.6125733790	-0.5350677816
H	-6.4922456912	-1.4744960589	-0.3788518488
H	-4.9681312991	2.5377271820	-0.6258942122
C	-2.3558132360	1.8415385313	-0.0805959170
C	0.0143931809	1.8080854890	0.1731631189
C	-2.3414999537	3.2275490886	-0.2165372427
C	0.0548275634	3.1980998572	0.0373884240
C	-1.1242857529	3.9250171540	-0.1555216091
H	-3.2670500221	3.7721323387	-0.3666198099
H	1.0081341983	3.7138491716	0.0857796833
N	-3.3522899119	-0.3507856575	0.0631590252
N	-1.1921650907	1.1773723813	0.1200537625
O	-1.0208016213	-2.8547373322	0.7796607725
C	-1.5864887447	-3.7240445663	0.0021551349
C	-1.0894747918	-5.1699140025	0.2665357498
O	-2.4134733749	-3.5312180696	-0.8756265378
F	-1.6198101596	-6.0338359461	-0.6065010299
F	0.2540737233	-5.2350176597	0.1588322391
F	-1.4202323742	-5.5775079028	1.5105461713
C	-7.3066699879	1.1311908590	-0.8446674718
H	-7.8328329031	1.3874809868	0.0841019632
H	-7.2660707949	2.0338608386	-1.4618068049
H	-7.9045180998	0.3768801700	-1.3643391086
C	-1.0939187107	5.4220530879	-0.3247947830
H	-1.1191892505	5.6811292883	-1.3910970221
H	-1.9612395192	5.8935221214	0.1481069554
H	-0.1844697516	5.8537519397	0.1018571465
H	-0.1025374919	-3.3300583027	2.1089655919
O	0.5868928236	-3.6592937372	2.7556848035
C	0.0401429221	-4.1623963429	3.8416699145
C	1.1241828947	-4.8070406366	4.7345684122
O	-1.1301104370	-4.1734301390	4.1517642328
F	2.1398157573	-3.9558935188	4.9608293180
F	0.6065014440	-5.1740547922	5.9132887262

F	1.6243364705	-5.9029679516	4.1312997575